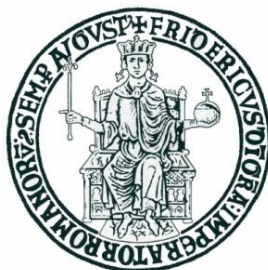


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DIPARTIMENTO DI INGEGNERIA CHIMICA

DOTTORATO DI RICERCA IN INGEGNERIA CHIMICA
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Evaluation of organic micropollutants and fine particles in vehicle exhausts and in ambient air

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Chapter 1

INTRODUCTION

The incredible increasing of the number of vehicles circulating in the Italian cities, occurred in the last fifteen years, is the main reason for still considering the traffic as the most important source of gaseous and particle pollutants in the urban atmosphere. The Automobile Club d'Italia has estimated that, in the period 1996-2009, the Italian circulating fleet grew of almost 76 %; almost 62% is the increment of the total passenger cars (ACI, 2010). The European statistic department states that in 2008 the total number of vehicle circulating in Italy related to the number of inhabitants was higher than the average data of EU-27 countries (European Commission, 2009). In Italy, in fact, at that date, there were 598 number of passenger cars per 1000 inhabitants respect 464 of the EU-27 countries.

Moreover, according to the ANCMA (Associazione Nazionale Ciclo Moto Accessori), which is the official Italian association of two- and three-wheelers manufactures, in the last 10 years there was an increasing of almost 10% of the circulating two-wheelers in the Italian cities. In 2010, in fact, almost 10 millions of two wheelers (mopeds and motorcycles) circulate in Italy (ANCMA, 2010). The association of Motorcycle Industry in Europe (ACEM) states that Italy is the European country with the highest number of powered two wheelers (PTW), followed by Germany, Spain and France (6, 5 and 3 millions of PTW respectively) (ACEM, 2010). The reason of this Italian supremacy probably lies in the fine weather which allows the use of PTW during the major part of the year and also in the traffic congestion of the city centre which encourages people to choose a motorcycle for faster moving.

The large volume of on road vehicles balances and deletes the positive effects in terms of exhaust emissions coming, in the last years, from the technological improvements regarding the engine combustion efficiency, the fuel quality and the after-treatment device performances. The urban air quality, in fact, is still greatly influenced by the elevated traffic volume, whose negative effects on the air pollution are made worse by the type of driving pattern enforced to the vehicle in a congested traffic situation. Continuous stop and go and cold starting greatly elevate the exhaust emission because of not properly working after treatment devices for pollutants abatement. Moreover, the presence of an high percentage of PTW contributes to increase the pollution level in

urban areas because they are mainly used for short distance travels in the cities and because they present high emissions compared to the other vehicle classes.

The pollution source from traffic is responsible of the worsening of urban air quality due to the increased concentrations of a lot of species very dangerous for environment and human health. Among these, the most critical pollutant is represented by particulate matter (PM₁₀ – particulate matter with the diameter lower than 10µm); in many Italian cities the contribution from road traffic to the PM concentration was estimated to be almost 60% (Taurino, 2009). PM₁₀ ambient air levels often overcome the actual standard limit. Moreover, due to the major hazard of fine particles, a PM_{2,5} (particles with an aerodynamic diameter less than 2,5 µm) standard limit was introduced by air quality legislation. Although the air quality network is not yet fully conformed for PM_{2,5} measuring, the first measurements confirm the elevated concentrations also for the fine fraction of particulate.

Air pollution coming from vehicle exhaust involves a quantity of organic compounds, generally indicated as organic volatile compounds, which include carcinogenic species. These compounds, although present in small concentrations, represent a real hazard for humans due to their demonstrated carcinogenic potential (such as benzene and benzo(a)pyrene). Moreover, they play a central role in the photochemical reactions promoting the formation of tropospheric ozone. Despite the gaseous physical state and the high reactivity in the atmosphere, the life time of some compounds can be extended through the condensation and agglomeration processes leading to particulate formation.

A lot of studies are available in the literature on the adverse health effects of air pollution on humans and environment which motivate a comprehensive field study to characterize the influence of traffic generated emissions on the temporal and spatial variability of air pollutant concentrations in the near-road environment. Health studies have indicated that populations near roads have an increased risk for a number of adverse effects (Venkatram et al., 2009). According to several epidemiological studies, children are more susceptible to air pollution than adults due to their increased respiratory rate and immature host defence mechanisms, which lead to the increased absorption of air pollutants (Yogev-Baggio et al., 2010, Akinbami et al., 2010). Exposure to air pollution, in fact, was found to increase the number of asthmatic children residing in urban areas (Islam et al., 2007) thus supporting a causality relationship between air pollution and asthma.

Indeed, due to very dangerous effects of such pollutants for human health and environment, the environmental policy carries out some safety measures (mainly the closing to circulation in some urban areas for all vehicles or for the most emissive ones) every time that the standard limit values of pollutants concentrations in air are largely exceeded.

In order to improve the actions for air quality safeguard, it becomes very important both to characterise the pollution source in terms of quantity and quality of emissions at the exhaust of the several in-use vehicle technologies and to establish the real contribution of road traffic to ambient air pollutant concentrations. Although the role of on road traffic to air pollution is indisputable, in fact, the real contribution of single pollutant to ambient air concentration is difficult to estimate because of physical and chemical processes occurring in atmosphere between the different species.

This topic becomes more and more complicated if considering the lack of emission data for the so called “unregulated” compounds, i.e. compounds not regulated by legislation for vehicle type-approval. Up to now, the different species included in volatiles organic compounds are unregulated at the vehicle exhaust, such as the particle number concentrations which will become “regulated” starting from 2011.

The experimental work which will be exposed in this thesis is framed in this contest. The detailed goals which the present work would reach will be discussed in the next section.

1.1 The aim of the thesis

This research activity starts from the needs to characterise the air pollution level of two pollutant classes (VOCs and fine particles) directly involved in global warming and characterised by an high risk for human health. In the urban environment, the air concentration of these pollutants is strictly related to vehicle exhaust. The correlation between the pollution source and the air quality is difficult not only for the complexity of physical and chemical processes occurring in the atmosphere but also because of the lack of exhaust emission factors especially for the unregulated pollutants and for new technology vehicles.

This experimental work is aimed to carry out a comprehensive characterisation of volatile organic compounds and fine particles at the vehicle exhaust and in the ambient air of several urban sampling sites in Napoli.

The main aims of the project are:

- ✓ To characterise physical and chemical properties of particulate sampled at the exhaust and in ambient air through an accurate and reliable methodology for the measurement of mass, number, size distribution and polycyclic aromatic hydrocarbons (PAHs) content.
- ✓ To characterise the behavior of different vehicle technologies regarding the particulate emissions.
- ✓ To improve the database of these exhaust unregulated emissions through experimental measurements of different vehicle technologies.
- ✓ To assess the ambient air concentration of BTEXs (benzene, toluene, ethylbenzene and xylenes) and fine particles in both open and road tunnel urban sites.
- ✓ To outline the air pollution in Napoli, highlighting the variation in the several sampling sites.
- ✓ To find a correlation between the exhaust pollution source and the air concentrations of BTEXs, PAHs and particle number in the traffic urban sites.

The methodology applied to realize this research plan involved two parallel experimental programmes: one aimed to measure exhaust emissions and the other to evaluate ambient air concentrations.

Vehicle exhaust emission factors were evaluated by executing experimental tests on chassis dynamometer on a fleet including 20 in use vehicles, each characterised by a different engine technology and type approval stage. For the air quality monitoring, in situ sampling were realised in several sites of Napoli city: urban and sub-urban sites and road tunnels. The road tunnel offers the advantage of excluding any other pollution source and any photochemical reaction because of the absence of sunlight (El Fadel, 2001). For this reason, the air concentration could be directly correlated to traffic emissions and is often considered representative of emission levels.

Particulate and PAHs analyses were carried out both in vehicle exhaust and in ambient air, whereas BTEXs measurements were realized only in ambient air. Detailed measurement and analysis methodologies will be provided in Chapter 3.

Chapter 2

VOLATILE ORGANIC COMPOUNDS AND FINE PARTICLES

This section discusses about the characteristics of Volatile Organic Compounds (VOCs) and particulate, highlighting, first of all, the risks of both pollutants for the environment and human health (Section 2.1). Moreover, the contribution from vehicle exhaust will be assessed in the section 2.2 through a review of the literature on this theme. Finally, the legislation about the standard limit for both pollutants at the vehicle exhaust and in the ambient air will be presented in the Section 2.3.

2.1 The risks for the environmental and the human health

The great interest for Volatile Organic Compounds (VOCs) measurement in ambient air is due to their carcinogenic and mutagenic effects on organism and human health and to their decisive role in photochemical smog. Photochemical smog is originated from the photochemical reaction of NO_x (NO+NO₂) and volatile organic compounds (VOCs) in the presence of sunlight. It is chemically characterized by a high level of oxidant compounds, mainly O₃. In urban areas, where NO_x and hydrocarbon emissions from traffic are high, O₃ tends to accumulate rapidly (Han and Naeher, 2006). The concentration of O₃ has a considerable effect on the oxidizing capacity of the troposphere, which affects human health by causing symptoms such as irritated eyes, cough, headache, lung inflammation. O₃ is also toxic to plants, leading to a decrease in vegetation, and associated with the corrosion of urban structures.

The European legislation has indicated a list of main ozone precursor in the Directive 2002/3/CE (Table 1), which are recommended to be measured in order to analyze their trends and to check the efficiency of emission reduction strategies (Dir. 2002/3/EC, 2002).

In case of long term exposure, VOCs may also represent a potential threat to human health, leading to mutagenic and carcinogenic effects. Benzene and 1,3-butadiene, for example, are classified by International Agency for Research on Cancer (IARC) as carcinogenic to humans (group 1) (IARC,

2010). They can also affect the nervous, immune and reproductive systems, being responsible for feelings of fatigue, headaches, dizziness, nausea, lethargy and depression (Weschler and Shields, 1997; Rumchev et al., 2004; Baroja et al., 2005; Ulman and Chilmonczyk, 2007).

This thesis has focused the attention on a sub-group of VOCs: the sum of Benzene, Toluene, Ethylbenzene and Xylenes isomers (BTEX). These compounds are all classified as ozone precursor.

| | |
|-----------------------|-------------------------------|
| ethane | isoprene |
| ethylene | n-hexane |
| acetylene | i-hexane |
| propane | n-heptane |
| propene | n-octane |
| n-butane | i-octane |
| i-butane | benzene |
| 1-butene | toluene |
| trans-2-butene | ethylbenzene |
| cis-2-butene | m-xylene |
| 1,3-butadiene | p-xylene |
| n-pentano | o-xylene |
| i-pentano | 1,2,4-trimethylbenzene |
| 1-pentene | 1,2,3-trimethylbenzene |
| 2-pentene | 1,3,5-trimethylbenzene |

Table 1. Main VOCs ozone precursors according to the Directive 2002/3/CE

Owing to their common chemical characteristics, they are often considered as a VOCs sub-group; they are present into liquid fuels and are emitted into the urban atmosphere as components of vehicle exhaust and by gasoline evaporation and spillage (Yassa et al., 2006). Benzene could also be produced over three way catalyst by dealkylation reaction occurring under very rich condition (for example during rapid acceleration or high road load).

Particulate matter emitted by mobile sources is responsible of adverse health effect and environmental problems such as global warming. Carcinogenic effect of particulate is strictly dependent on dimension of particles: smaller particles are able to penetrate deeper into human lungs, posing serious health effects, such as asthma and bronchitis. Figure 1 illustrates the deposition rate in the different pulmonary regions according to particle size. This figure clearly illustrates that in the region 5-20 nm the retention of inhaled nanoparticles is nearly 90% and more than 50% are deposited in the alveolar region. Particle size distribution thus has a major impact on the pulmonary deposition site. Due to a very large specific surface and very high reactivity of

nanoparticles, the biological behavior of nanoparticles and their effects on living organisms can become totally different when particle size decreases. Nanoparticles may, in fact, penetrate cells and tissue, enter the capillary blood vessels in the lungs, be transported by the blood stream to other organs, cause oxidative stress in cells, cause inflammatory reactions in cells (see Figure 2).

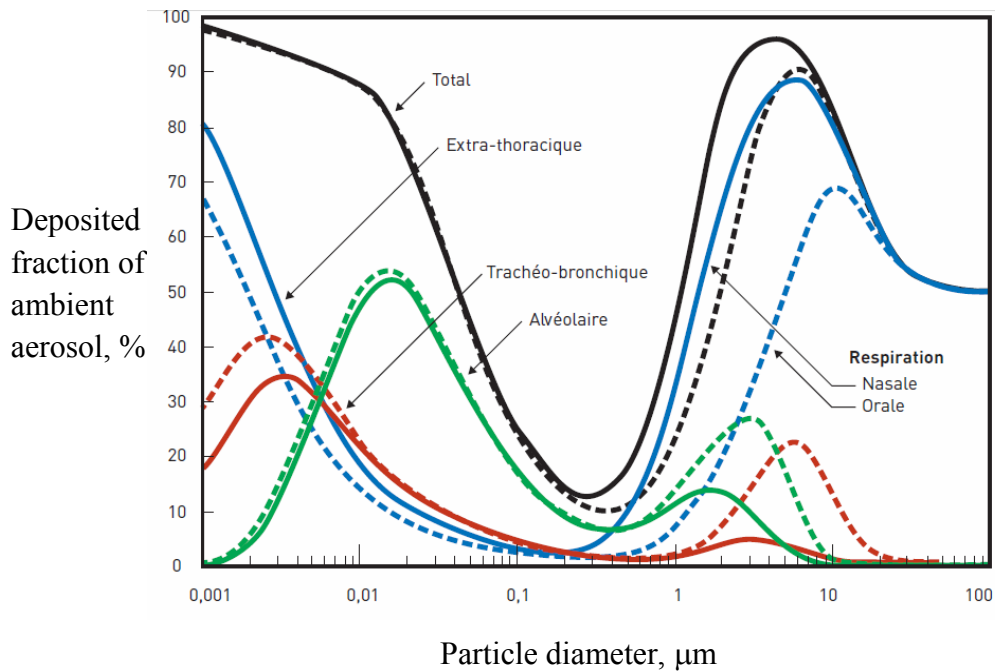


Figure 1. Aerosol deposition in human lungs as a function of the particle diameter (INRS, 2005)

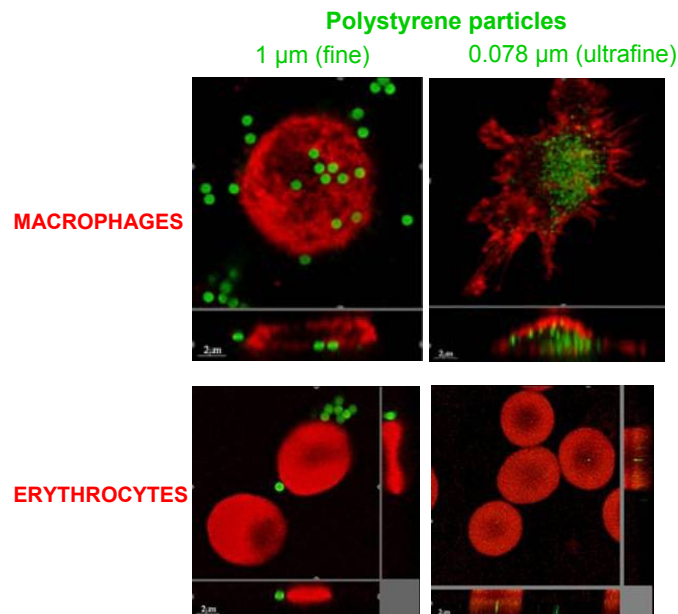


Figure 2. Interaction between polystyrene nanoparticles and human cells (Gehr, 2008)

Even though the mechanism of PM health effects is still incompletely understood, a recent hypothesis relates toxicology of PM to redox activity. Previous studies have demonstrated that a high correlation between redox activity and several PM species (such as elemental carbon, organic carbon, low molecular weight PAHs) exists. Introduction of three way catalytic converters and particulate filters has, in fact, reduced PM emissions but particle number (PN) have not been equally reduced mainly due to nucleation occurring downstream the after-treatment devices. The particulate filter, in fact, has a low trap efficiency towards volatiles included in the nucleation mode. Moreover, modern engines emit smaller primary particles than older engines. This is the reason for a not equal decreasing in redox activity (Geller et al., 2006).

For these reasons, the number and the size distribution is one of the key characteristics of particulate matter. Current ambient air quality standards establish limit values for PM_{2,5} (particles with aerodynamic diameter lower than 2,5 μm) and PM₁₀ (particles with aerodynamic diameter lower than 10 μm). The PM_{2,5} fraction is sometimes referred to as fine particles, while the difference between PM₁₀ and PM_{2,5} as coarse particles. An alternative approach in classification of the particles is to consider location of the modes in particle size distributions, which could relate to the contribution from different pollution sources. A mode may be defined as a peak in the lognormal function of the number or mass distribution. An example of lognormal distribution is reported in Figure 3.

The areas below the three curves correspond to the total particle number, surface and volume, respectively. Three terms were introduced for aerosol distribution in terms of modal diameters: nucleation mode ($<0.1\mu\text{m}$), accumulation mode ($0,1-1\mu\text{m}$) and coarse mode ($>1\mu\text{m}$). Sometimes the nucleation mode is identified in the region of diameters lower than $0.01\mu\text{m}$, and particles belonging in $0.01-0.1\mu\text{m}$ are classified as belonging to Aitken mode.

Physical properties of particulate are only one aspect of risk assessment for this pollutant. The other very important topic concerns the chemical composition, often very complex to be characterised. Particulate, in fact, includes numerous compounds both inorganic and organics. Particles belonging to the accumulation mode are formed by a carbonaceous core with condensed organic compounds. Smaller particles, instead, belonging to nucleation mode are mainly composed by volatiles or sulphates. This means that the aerosol is a great carrier of condensed hydrocarbons into human lungs, causing serious effects to the human health. For example it was largely demonstrated that the

organic fraction of aerosol acts as adjuvant during allergic sensitization and can also induce acute asthma exacerbations (Li et al., 2003).

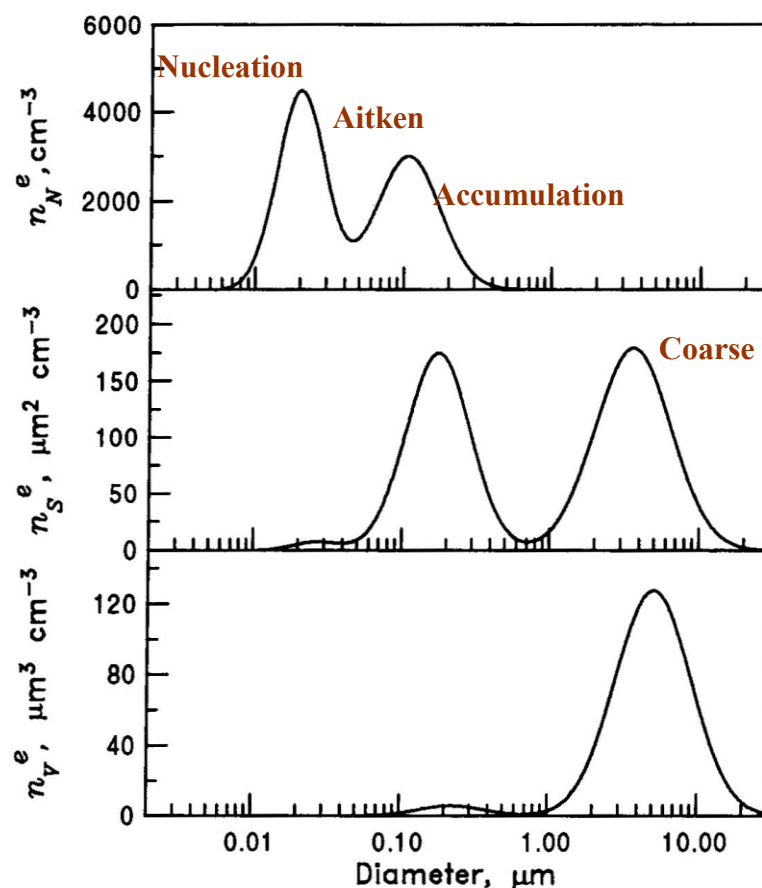


Figure 3. Log normal distribution of number, mass and volume of particles

Organic particulate matter pollution in the urban area was the subject of a large number of studies carried out during the last 15 years. These studies have highlighted that organic fraction is strongly dependent by season. This seasonal change is a consequence of a different partitioning of semi-volatile organic compounds due to different ambient temperature (Grieshop et al., 2006, Zakey et al., 2008, Funasaka et al., 1998, Handler et al., 2008). For this reason, a growing number of research studies are focused on assessing the chemical composition of organic aerosol (Wang et al., 2006).

Among the condensed hydrocarbons, a big attention is toward the Polycyclic Aromatic Hydrocarbons (PAH). A number of these components are significant sources of human exposure to mutagenic and carcinogenic chemicals that may also cause oxidative and DNA damage that can lead to reproductive and cardiovascular effects. (Lewtas , 2007). The class of PAH includes several

hundred individual compounds defined to be composed of two or more fused aromatic rings. Due to their very different values of volatility, PAHs can be released both supported onto the particulate matter and/or in the gas phase. Although this gas/solid partitioning is related to many different variables (the liquid vapor pressure, the ambient temperature and the size, chemical composition and surface area of the PM), several studies have demonstrated that the most volatile compounds with two or three aromatic rings, are mainly released in the gas phase, while compounds containing more than three aromatic rings, are generally associated with the PM emission (Liu et al., 2007). According to Andreou et al, 2009 and Valavanidis et al., 2006 a percentage equal to 98% of the identified and quantified PAHs was found in PM_{2.5}.

Moreover, the use of the new fuels such as water diesel emulsions and biodiesel blends produces a shifting of particulate size distribution towards the ultrafine region, with a consequent high content of PAHs (Zanini et al., 2006).

2.2 The contribution of vehicle exhaust to the ambient air concentration

Vehicle exhausts greatly contribute to VOCs and particulate concentration in urban ambient air.

Previous studies have demonstrated that the concentrations of VOCs are highly correlated with traffic volume at most urban monitoring sites, indicating that, in urban areas, they are primarily emitted by mobile source (Curren et al., 2006, Hung-Lung et al., 2007).

VOCs are mainly emitted by spark ignition (SI) vehicles characterized by a higher operating fuel/air ratio in the combustion chamber in respect to compression ignition (CI) ones. They are originated from the unburned fuel and the lubricating oil which escape the oxidation reaction occurring over the catalyst. The oxidation of the unburnt hydrocarbons needs of the oxidant whose presence is not ensured during rich operating condition (i.e speed acceleration, full load). It has to be pointed that the VOCs emissions during these catalyst failures became, in the years, more and more negligible because of the very precise control strategy of three-way catalyst mounted at the exhaust of the modern SI vehicles.

Two wheelers of small engine capacity (such as mopeds), despite belonging to SI vehicles, make exception: exhaust after-treatment technology is not so sophisticated to ensure a good pollutants abatement as happens for the passenger cars (Spezzano et al., 2008). Sometimes, the after-treatments

are even absent. The reasons lie in the costs which have to be low to make the vehicle competitive and in the reduced available space. Moreover, the poor technology is often associated to poor vehicle maintenance by the owners (Lin et al., 2008).

Previous studies about the correlation between the traffic volume and the VOC ambient air concentrations have demonstrated that the two-wheelers play a decisive role in the air quality. In particular, benzene concentration in air is greatly influenced by two wheelers emissions in city, such as Bangkok, where the number of the vehicles, belonging to this category, is particularly high (Leong et al., 2002).

The emission of VOCs from vehicle exhaust is related not only to the properly working exhaust catalyst but also to the cold start phase which represents the main cause for hydrocarbon emissions. During cold start two effects add up: the enrichment of combustion mixture for enhancing the combustion process and the not working of catalyst due to the temperature lower than light-off (temperature which ensures the 50% of conversion efficiency over the catalyst). It was measured that almost 90 % of total emission during a driving cycle is emitted during the cold start. Temporal and spatial duration of cold start phase establishes the VOCs emissions (Weilenmann et al., 2009).

Cold start duration greatly influences also the benzene emissions. Heeb et al. have demonstrated that, despite the total emission reduction of benzene and alkyl benzene when moving from the oldest technologies to the newest ones, the contribution deriving from cold start was not so reduced (Heeb et al., 2003). The cold start contribution becomes decisive in urban areas where the vehicles are used for short distances and at low speed. In these conditions the cold start duration is not negligible respect on the whole urban pattern.

Particulate is, instead, a typical pollutant emitted at the exhaust of CI and gasoline direct injection (GDI) vehicles. Exhaust particulate is composed by a semi-volatile fraction with a mode diameter smaller than 50 nm (nucleation mode), and by a non-volatile portion (between 50-200 nm belonging to the accumulation mode) formed by particles with an elemental carbon core and low vapour pressure hydrocarbons and sulphur compounds adsorbed on their surface (Maricq, 2007). Semi-volatile fraction is mainly produced by vapors cooling and condensing in the exhaust lines, whereas carbon particles are originated by combustion process. In other words, both combustion and ambient condition control the two fractions of exhaust particulate.

The introduction of diesel particulate filter (DPF) at the exhaust of modern diesel vehicles has markedly reduced the particle mass and number emissions (Bergmann et al., 2009, Dwyer et al.,

2010a). The so called wall-flow filters which force the flow gas to pass through the walls of the filters may have a filtration efficiency higher than 99%.

Despite the enormous advantages for PM reduction, there is an open issue regarding the DPF operation: the regeneration process. This process indicates the cleaning of filter through the oxidation of the trapped carbon to carbon dioxide by NO₂ (passive regeneration) or by O₂ (active regeneration). The passive regeneration is continuously guaranteed because the NO₂ is produced by a pre-oxidation catalyst; the active one is controlled by post fuel injection in the combustion chamber which increases the exhaust temperature to allow the oxidation of carbon with oxygen. During both regenerations, a great production of fine particles was observed. If the regeneration is active, the fine particle emissions are mainly constituted by volatiles derived by the fuel enrichment (Dwyer et al., 2010b).

According some experimental studies, the content of PAHs in particle phase is also reduced downstream of the DPF, especially when the filter is catalyzed (Vouitsis et al., 2009).

As already highlighted the organic fraction bounded to particle phase is object of several studies which are aimed to chemically characterize the exhaust particulate and also to find a common chemical aspect between the exhaust and ambient aerosol. Most of these studies were carried out under urban road tunnel. Roadway tunnel studies are well suited to determine an average vehicular exhaust profile representative of total vehicular fleet at operating conditions with little interference from laboratory operating conditions (El Haddad, 2009).

2.3 European legislation for air quality and vehicles type approval

All the VOCs considered in this experimental work (PAHs and BTEXs) are not subjected to any regulation at the vehicle exhaust. For this reason, they belong to the so called “unregulated compounds”. The European legislation for the vehicle type-approval only states the standard limits for the sum of all the hydrocarbons detected by the Flame Ionization Detector. Starting from Euro5a stage, coming into force on September 2009, it is compulsory to measure also non-methanic hydrocarbons (NMHC) for gasoline motorization.

The European air quality legislation states a limit value for the annual average to benzene concentration. This limit is 5 µg/m³ in year 2010 (Dir. 2000/69/EC, 2000). Moreover the European

directive 2004/107 (Dir. 2004/107/EC, 2004) states a target value of 1 ng/m^3 for the annual average of the benzo(a)pyrene concentration in air.

The legislation for vehicle type approval established from Euro1 to 4 stages a decreasing limit of the mass of particulate (PM) for diesel vehicles (Figure 4). The actual Euro5a stage (come in force on september 2009) imposes the emission limit of particulate matter PM of 5 mg/km not only to diesel vehicles but also to gasoline direct injection (G-DI) ones (Reg. 715/2007, 2007, Reg. 692/2008, 2008). The procedure for PM measurement will be detailed in the next section 3.1.1. Moreover, the same regulation introduces, for the first time, a limit for total solid particle number (PN) for diesel and G-DI vehicles. This limit of 6×10^{11} particles/km will be compulsory starting from year 2011 with Euro5b legislation stage. The procedure for PN measurements is known as PMP method (Economic Commission, 2008) and involves a volatile particle remover and a particle counter positioned downstream of the dilution tunnel used in a chassis-dynamometer test (see section 3.1.1 for details).

Regarding the particulate in the ambient air, European legislation states limits for PM₁₀ and PM_{2.5}. The Directive 1999/30 (Dir. 1999/30/EC, 1999) established the limits of PM₁₀ as annual average and daily average ($20 \text{ } \mu\text{g/m}^3$ and $50 \text{ } \mu\text{g/m}^3$ in the year 2010). The Directive 2008/50/ (Dir. 2008/50/EC, 2008) establishes a target of 25 micrograms per cubic meter to be reached in the year 2015 for the more dangerous fine particles PM_{2.5}.

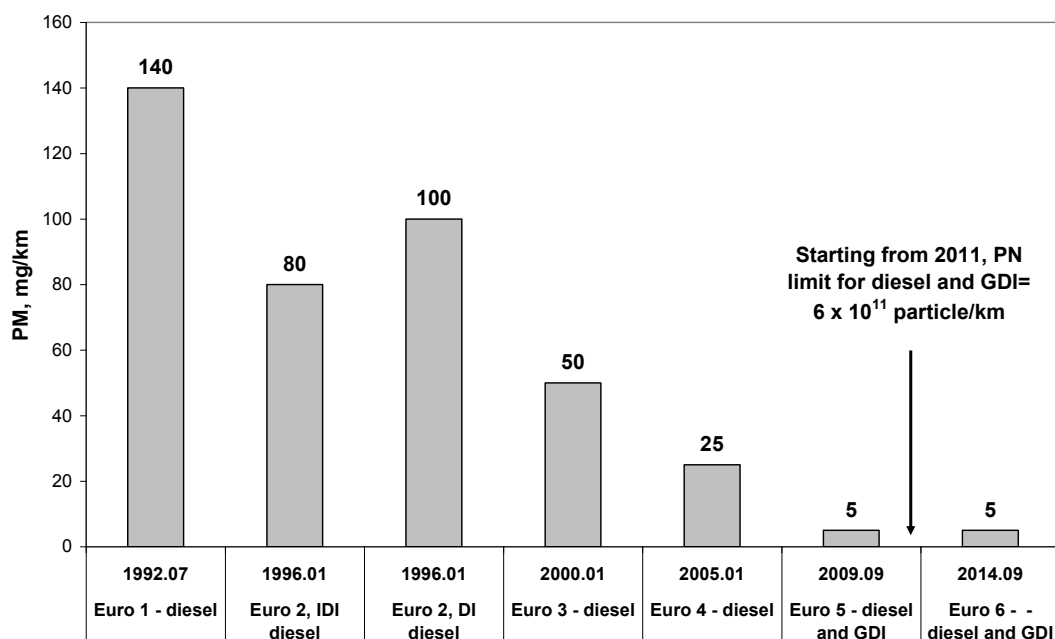


Figure 4. PM emission limit from Euro1 to Euro 6

Chapter 3

EXPERIMENTAL ACTIVITY DESCRIPTION

In this section, the measurements procedures and the analysis methods will be detailed. Because of the diversity of experimental tests carried out to characterize the vehicle exhaust and the ambient air, the experimental set-up for measurements of exhaust emissions will be exposed separately by that used for ambient air monitoring. In particular, the section 3.1 will expose the instruments used to test the vehicles on chassis dynamometer together with the characteristics of the vehicles and of the driving cycles. The experimental campaigns for ambient air monitoring in Napoli and the relative measurement techniques will be, instead, discussed in the section 3.2.

3.1 Measurements at the vehicle exhaust

3.1.1 Experimental set-up

The measurements at the vehicle exhaust were realised on the chassis dynamometer in the laboratory of Istituto Motori of National Research Council equipped with two roller test benches for testing both two- and four-wheeler vehicles. The main advantage of dynamometer measurements is the better repeatability of tests compared with on-road ones which, instead, have the characteristic to be more realistic.

During the laboratory test, the vehicle is positioned on the chassis dynamometer equipped with an electric engine which is calibrated in order to offer the right vehicle inertia and the right road load resistance as a function of the vehicle speed. The emission factors of gaseous and particle pollutants are evaluated by measuring all the pollutant concentrations during the execution of a driving cycle (speed vs time). The driving cycle is displayed to the driver by the driver's aid unit. This unit saves the real speed trace for the comparison with the theoretical one in order to evaluate the percentage of errors occurred during the execution of driving cycle. The laboratory of Istituto Motori is also equipped with an automatic driving system (Horiba-ADS), useful to perform very repeatable tests. The fan in front of the vehicle is used for cooling the engine and the wheelers, simulating the action of air during on-road real driving. Figure 5 shows the scheme of a dynamometer laboratory for four

wheelers vehicles. The set-up laboratory for two-wheelers tests is analogous to that showed in Figure.

During the execution of driving cycle, the raw exhausts are sampled and diluted by ambient air in order to simulate the dilution in the real on-road use and also to avoid the water concentration before the gases analysis.

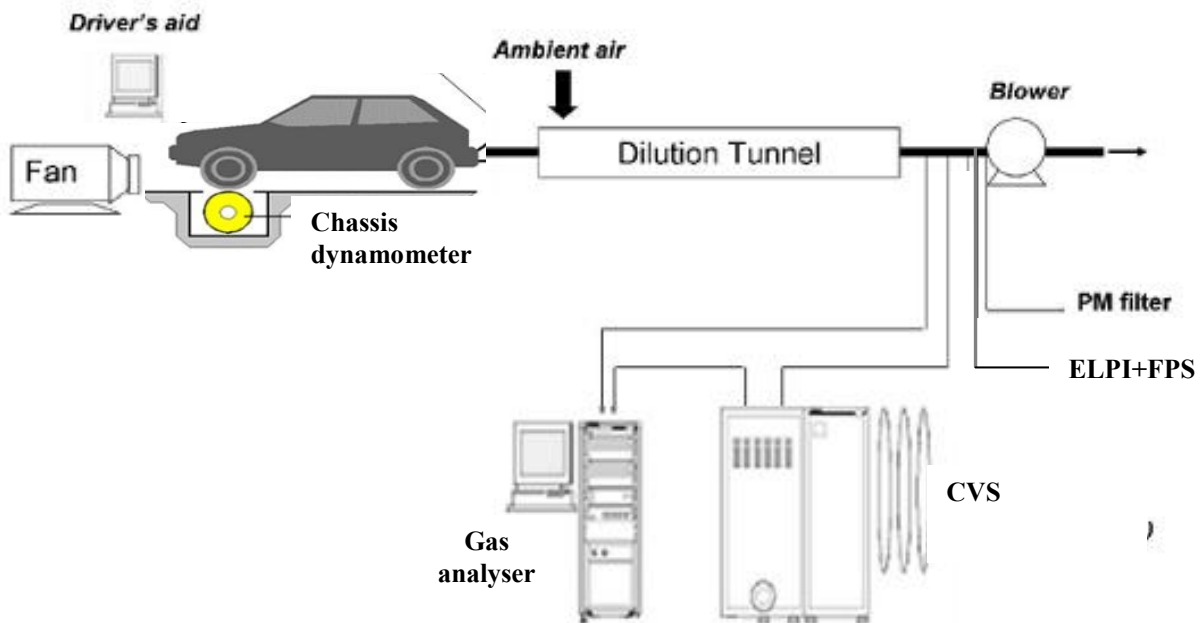


Figure 5 Scheme of dynamometer test cell for vehicle emission measurements

The total diluted flow is set constant by a positive displacement pump (PDP) belonging to a constant volume sampling device (CVS). A portion of the total flow is spilled and sent to a Tedlar sampling bag during the whole duration of the driving cycle. At the end of the sampling phase the content of the sampling bag is analyzed to measure gaseous concentration of CO, CO₂, HC, NO_x and O₂. The four wheelers laboratory is equipped with an Horiba Mexa 7200H bench whereas that for two wheelers by an AVL AMA-4000 bench. The measuring techniques of gas analyzers are suggested by European legislation for type-approval of vehicles: CO and CO₂ are measured by Non Dispersive InfraRed detector (NDIR), HC by Flame Ionization Detector (FID), NO_x by Chemiluminescence (CLD) and O₂ by paramagnetic. In order to evaluate the background pollution level of the dilution and combustion air, a sampling bag is filled with the dilution air during the driving cycle and analyzed at the end of the test. By knowing the gases concentrations, the total flow rate of CVS and the kilometers driven during a specific driving cycle, it is possible to evaluate the emission factors of each pollutant expressed as g/km. Moreover, the fuel consumption is

estimated by a carbon balance applied to the species containing the carbon atoms, making the hypothesis of a stoichiometric combustion.

Particulate was characterized in terms of total mass, total number, size distribution and PAHs content.

Particle number (PN) and distribution is measured by an Electric Low Pressure Impactor (ELPI) by Dekati Ltd. It is able to count, in a continuous way, the number of particles with the aerodynamic diameter between 7 nm to 10 μm , collected on twelve dimensional stages. ELPI allows the collection of particles samples on the twelve aluminum foils, each associated to a specific dimensional stage, in order to carry out some physical and chemical analysis on the trapped particulate. The particle sizing is allowed by the geometry of the impactor which collects the bigger particles (previously charged by a corona discharge and then accelerated by a high voltage electric field) on the top of the classifier and the smallest ones on the bottom side. ELPI is coupled with a Fine Particle Sampler (FPS) by Dekati Ltd in order to dilute and so lower raw particle concentration.

The FPS unit is composed by a double diluter including a porous tube and an ejector, to perform a dilution ratio between 10 to 100, at temperatures ranging from the ambient one up to 250°C. The sampling probe of FPS can be positioned on the raw exhaust flow or at the end of dilution tunnel, depending on the concentration levels to be measured. In both cases the flow rate of total gaseous stream has to be measured for estimating emission factor as number of particles for kilometre driven. For diluted measurements, the flow rate is given by CVS parameters, whereas in the raw measurement a Pitot tube flow meter of the Sensors Semtech-D portable emissions measurement system is used to measure second by second the volumetric exhaust flow rate.

Particulate Matter (PM) measurement is performed by following the gravimetric procedure suggested by European legislation for diesel vehicle type-approval.

A collection filter (Heat resistant borosilicate glass fiber coated with fluorocarbon (TFE) – Aerosol retention of 96.4% - Fiber Film Filter by PALL) is used to sample particulate contained in a portion of the diluted exhaust flow. The filter holder is positioned downstream of the dilution tunnel. The weight difference of the filter before and after the sampling gives the total mass emitted.

Collecting filters used for PN and PM quantification are then analysed to evaluate the content of some Polycyclic Aromatic Hydrocarbons (PAHs). In particular, filters are Soxhlet extracted and

analysed by Gas-Chromatography with Mass Spectrometer (GC-MS) to quantify PAHs content (US-EPA, 1999b).

Chemical characterisation of particulate sampled by ELPI was carried out with the extraction of collecting filters grouped in three size ranges. In particular, the twelve collecting filters were divided in three size groups which are separately analysed and characterised by the following dimensions.

Group 1 7 nm – 0.1 μ m

Group 2 0.1 μ m – 1 μ m

Group 3 1 μ m – 10 μ m

In other words, Group 1 examines the PAHs content in the nucleation mode, the Group 2 in the accumulation mode and the Group 3 in the coarse mode.

After sampling, the ELPI aluminium foils of the three size ranges, or the PM filter, were Soxhlet extracted with ciclohexane for at least 12 hours. The extract was then concentrated to 0,5 ml with rota vapour and pure-nitrogen flow. In order to evaluate the PAHs recovery efficiency, the standard mixture (Dr. Ehrenstorfer Mix 31) containing 5 deuterated PAHs (naphthalene D8, acenaphthene D10, phenanthrene D10, chrysene D12, perylene D12) was added to the sample before the Soxhlet extraction. PAHs analysis was realised with a gas chromatograph (HP 5890 Series II) coupled with a mass selective detector (HP 5971A). The GC/MS was equipped with an Agilent capillary column DB-5MS (30m x 0.25mm x 0.25 μ m). The sample volume of 1 μ l was on-column injected. The operative conditions of GC are: carrier gas: helium; Initial head column pressure: 70kPa; Initial temperature of injector and oven: 70°C; programme of temperature: 20°C/min up to 280°C-9 min at 280°C-20°C/min up to 310°C-2 min at 310°C. These chromatographic conditions allow the retention times to be below 22 min.

In order to delete the uncertainty coming from the exact injected quantity, an internal standard of four compounds (Acenaphthene-d8, Fluoranthene-d10, Benzo(k)fluoranthene-d12 and Benzo(g,h,i)perylene-d12) was added in a fixed concentration to the sample just before of the injection. Quantitative analysis, performed in single ion monitoring mode, was obtained evaluating the ratio between the instrumental response of 5 concentration levels of 2 standard mixtures (Dr. Ehrenstorfer Mix 45 and Mix 183) and the internal standard.

Table 2 reports the list of PAHs which are determined. The table also indicates the IARC (International Agency for Research on Cancer) classification for carcinogenicity. According to this classification benzo(a)pyrene (B(a)P) belongs to group 1 and so is carcinogenic to humans. Naphthalene, Benzo(a)anthracene, Benzo(b+k+j)fluoranthene, Chrysene, Indeno(1,2,3,c,d)pyrene, Dibenzo(a,h)pyrene and Dibenzo(a,i)pyrene are possibly carcinogenic to humans. Dibenzo(a,h)anthracene and dibenzo(a,l)pyrene are probably carcinogenic to humans.

| Compound | IARC Classification* |
|--|-----------------------------|
| naphtalene | 2B |
| acenaphtilene | 3 |
| acenaphthene | 3 |
| fluorene | 3 |
| phenanthrene | 3 |
| anthracene | 3 |
| fluoranthene | 3 |
| pyrene | 3 |
| benzo(a)anthracene | 2B |
| chrysene | 2B |
| benzo(b+k+j)fluoranthene | 2B |
| benzo(e)pyrene | 3 |
| benzo(a)pyrene | 1 |
| perilene | 3 |
| indeno(1,2,3,c,d)pyrene | 2B |
| dibenzo(a,h)anthracene | 2A |
| benzo(g,h,i)perilene | 3 |
| dibenzo(a,e)pyrene | 3 |
| coronene | 3 |
| dibenzo(a,h)pyrene | 2B |
| dibenzo(a,i)pyrene | 2B |
| dibenzo(a,l)pyrene | 2A |
| * Group 1: Carcinogenic to humans; Group 2A: Probably carcinogenic to humans; Group 2B: Possibly carcinogenic to humans; Group 3: Not classifiable as to its carcinogenicity to humans | |

Table 2. List of PAHs

The experimental results show that the mean recovery efficiency was lower than 50% for naphthalene D8 and acenaphthene D10; for this reason the quantitative analysis was realised starting from phenanthrene.

3.1.2 Vehicle description

The activity carried out within this experimental work has involved several resources provided by Istituto Motori-CNR for founding the experimental tests needed to evaluate the emission factors at the vehicle exhaust.

The tested fleet of in-use vehicles is characterized in Table 3. The table groups the vehicles first of all according to the category of mopeds, motorcycle, passenger cars and light-duty vehicles. In the same table the engine capacity and the type-approval stages are also indicated. Inside the same category the vehicles are differentiated for some technological topics, considered influencing for emission behavior.

In particular, the attention was focused for two-wheelers on the combustion type (2- or 4-stroke). Moped category includes both 2- and 4-stroke of different type-approval stages (Euro 1 and Euro2), whereas the motorcycle tested is equipped with a 4-stroke engine. The engine capacity of the motorcycle was specified because the type approval homologation differentiates the motorcycle with an engine capacity higher and lower than 150 cm³. The exact distinction will be reported in the following section about the driving cycles. This vehicle is particularly performing in terms of speed and power.

Concerning the four-wheelers, the engine type (compression ignition, spark ignition and hybrid) and fuel (gasoline, diesel and compressed natural gas) were considered the main highlighted characteristics. All the sub-groups, with the exception of hybrid and CNG categories, include two samples of vehicles.

It has to be noted that the compression ignition vehicles (both passenger cars and light-duty) were sub-grouped according the presence or not of the Diesel Particulate Filter (DPF). The presence of the DPF, in fact, is determinant for a sensible reduction of the particle emissions.

The Alfa Mito is the only tested Euro 5 vehicle; the DPF, in this case, is positioned very close to the engine exhaust in order to take advantage of the higher temperature for passive filter regeneration process. The DPF passive regeneration is, in fact, strictly dependent on the exhaust temperature

which promotes the oxidation reaction between the trapped particulate and the NO_2 , previously produced by engine-out NO . NO_2 is used as the oxidant agent because it lower the burning temperature of particulate to almost 300°C (instead of almost 600°C needed by oxygen), allowing the continuous filter regeneration at normal hot engine operation.

The other DPF-vehicles were conform to Euro 4 type-approval stage. They mount the diesel filter not so close to the engine exhaust.

All the DPF of the vehicles work with mixed strategy for filter regeneration (active/passive). Besides the promotion of passive regeneration process already described, the control strategy is able to actuate a regeneration process when the pressure drop over the filter reaches a limit value. The active regeneration involves the post-fuel injection in order to strongly increase the exhaust temperature and allow the oxidation of trapped carbon with oxygen.

| CATEGORY | TECHNOLOGY | VEHICLE | ENGINE CAPACITY, cm3 | Type approval year | TYPE APPROVAL STAGE |
|--|-------------------------------|-------------------------------------|----------------------|--------------------|---------------------|
| MOPEDS | 4 STROKE | VESPA PIAGGIO 4T 4V ¹ | 50 | | EURO 2 |
| | | HONDA ZOOMER ² | 50 | | EURO 2 |
| | | PIAGGIO LIBERTY ² | 50 | | EURO 2 |
| | | PIAGGIO ZIP ² | 50 | | EURO 1 |
| | 2 STROKE | KIMCO DYNK ² | 50 | | EURO 2 |
| | | MALAGUTI CIAK ² | 50 | | EURO1 |
| MOTORCYCLE >150CM ³ | 4 STROKE | MV AGUSTA BRUTALE ¹ | 989 | 2009 | EURO 3 |
| PASSENGER CAR | COMPRESSION IGNITION WITH DPF | ALFA MITO ³ | 1600 | 2010 | EURO 5 |
| | | NISSAN QUASHQUAI ³ | 1500 | 2009 | EURO 4 |
| | COMPRESSION IGNITION W/O DPF | FIAT 500 ⁴ | 1200 | 2008 | EURO 4 |
| | | FIAT ULYSSE ¹ | 2000 | 2003 | EURO 3 |
| | | FORD MONDEO ¹ | 2000 | | EURO 3 |
| | HYBRID ELECTRIC/GASOLINE | HONDA CIVIC ⁵ | 1400 | | EURO4 |
| | NATURAL GAS | FIAT PUNTO ⁵ | 1200 | | EURO 4 |
| | SPARK-IGNITION | FIAT PUNTO ⁵ | 1200 | | EURO4 |
| | | RENAULT MEGANE ⁴ | 1600 | | EURO3 |
| LIGHT-DUTY VEHICLE | COMPRESSION IGNITION W/O DPF | CHRYSLER VOYAGER ⁴ | 2800 | | EURO 4 |
| | | FIAT DUCATO ⁶ | 2300 | | EURO 4 |
| | COMPRESSION IGNITION WITH DPF | MERCEDES BENZ SPRINTER ⁷ | 2150 | | EURO 4 |
| | | IVECO DAILY ³ | 2800 | | EURO 4 |
| ¹ Project funded by BASF; ² Project funded by Italian Ministry of Environment; ³ Project funded by Italian Ministry of Transport; ⁴ CUNA Round Robin test; ⁵ Activities funded by internal resources; ⁶ Project funded by PRIN; ⁷ Project funded by Mobilab INTERREG III B ARCHIMED Project | | | | | |

Table 3. Characteristics of tested fleet

3.1.3 Driving cycles

The emission factors were measured during the execution of normalised and real driving cycles. The term “normalised” is referred to the driving cycle established by European legislation for type-approval procedure.

The type approval driving cycles are differentiated according to the vehicle to be tested. Starting from Euro 3 stage, the passenger cars and the light-duty vehicles have to be tested over the so called NEDC (New European Driving Cycle, showed in Figure 6) which is composed by an urban part (UDC) which includes 4 repetitions of an urban module and by an extra-urban phase (EUDC).

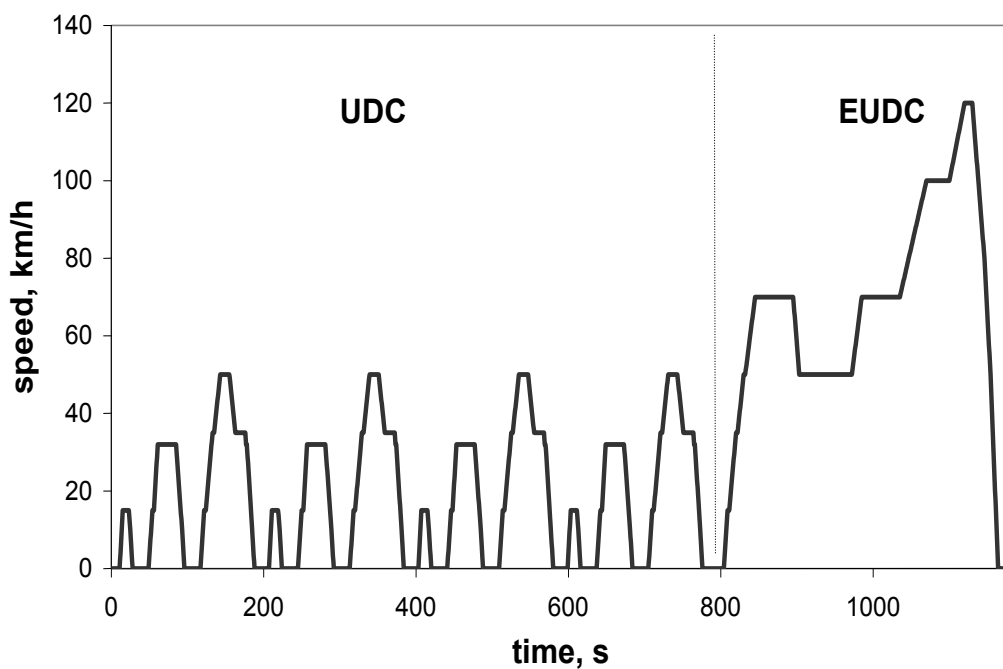


Figure 6. NEDC speed trace

The type-approval driving cycle for the two wheelers depends on the engine capacity; the 50 cm³ mopeds are tested during the ECER47 driving cycle, composed by 8 repetitions of a base module with the maximum speed of 45 km/h. The useful part for pollutant sampling covers the second half of the cycle. The first 4 modules, in fact, constitute the warming-up phase.

The motorcycle with engine capacity lower than 150 cm³, have to be tested, instead, during the ECER40 (6 repetitions of the same module of UDC driving cycle). When the engine capacity becomes higher than 150 cm³, an extra-urban part has to be added. The driving cycles for two wheelers are displayed in Figure 7.

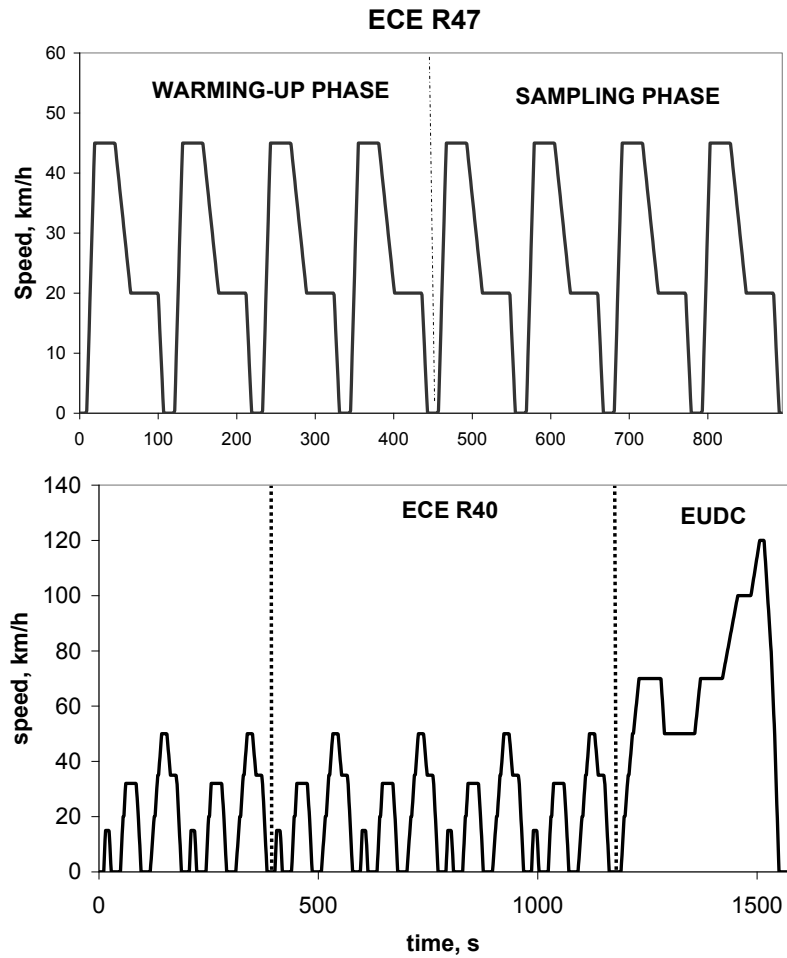


Figure 7. Speed trace of type approval driving cycles for two wheelers

The European legislation offered an alternative type approval driving cycle for Euro 3 motorcycles. This driving cycle, called WMTC (Worldwide Motorcycle Test Cycle) and plotted in Figure 8, arises from the necessity to harmonize the type-approval procedure around the world. It is composed by three different parts, each characterized by an own average speed. The legislation suggests a different procedure for the execution of the WMTC depending on engine capacity and maximum speed of the motorcycle to be tested. For motorcycle having a maximum speed lower than 120 km/h, the driving cycle speed is “reduced”.

Concerning the real driving cycles, almost all the experimental fleet was tested during the execution of the ARTEMIS driving cycles. These driving cycles were developed in the framework of the European Project ARTEMIS (Assessment and Reliability of Transport Emission Models and Inventory Systems) (TRL, 2005), in order to characterize the emission behavior of a vehicle during a real use.

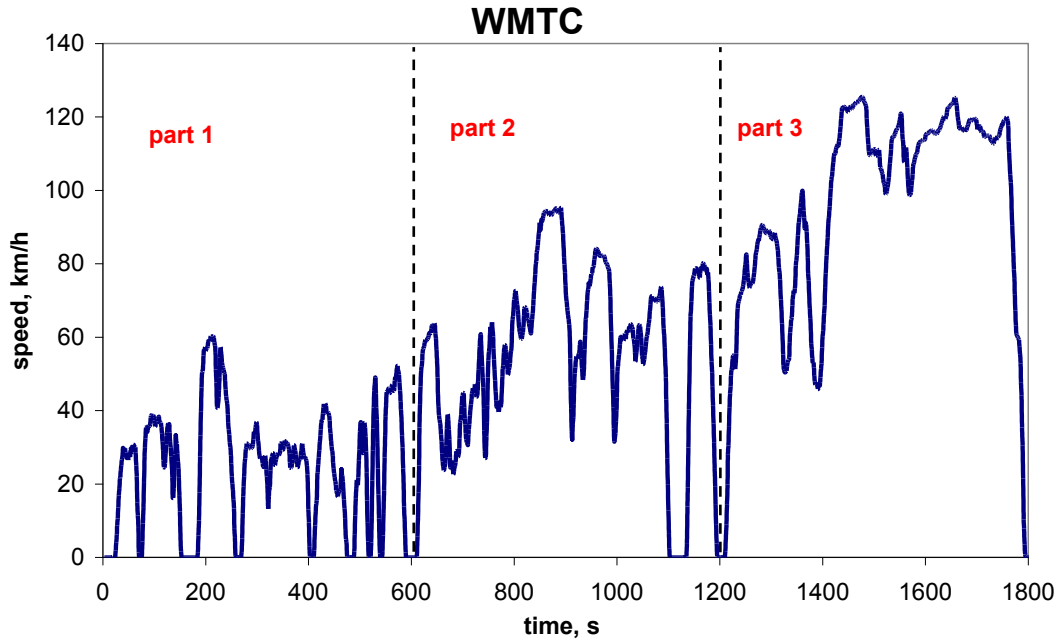


Figure 8. WMTC speed trace

The ARTEMIS CADC (Common Artemis Driving Cycle) includes three driving cycles called Artemis Urban, Artemis Rural and Artemis Motorway. These driving cycles represent several traffic situations, from congested to fluid, and are obviously characterized by an increasing average speed. They are characterized by rapid acceleration and deceleration which force the engine and the vehicle to work in some operating zones different from those of type-approval driving cycles. All the Artemis cycles have to be performed in hot starting condition; for this reason a pre-conditioning phase is present at the starting of cycle, during which all the samplings are off (Figure 9).

3.2 Measurement in ambient air

Ambient air monitoring is, instead, conducted with in-situ measurements. Even though they are dependent by traffic condition, the main advantage of this measurement is the absence of dependence by dilution process which in some cases (such as for particle number measurements) could deeply interfere with the measurements (Charron et al., 2003).

Two experimental campaigns were carried out to evaluate the ambient air pollutant concentrations in Napoli city. The first one was held in November-December 2009, the second one in May 2010.

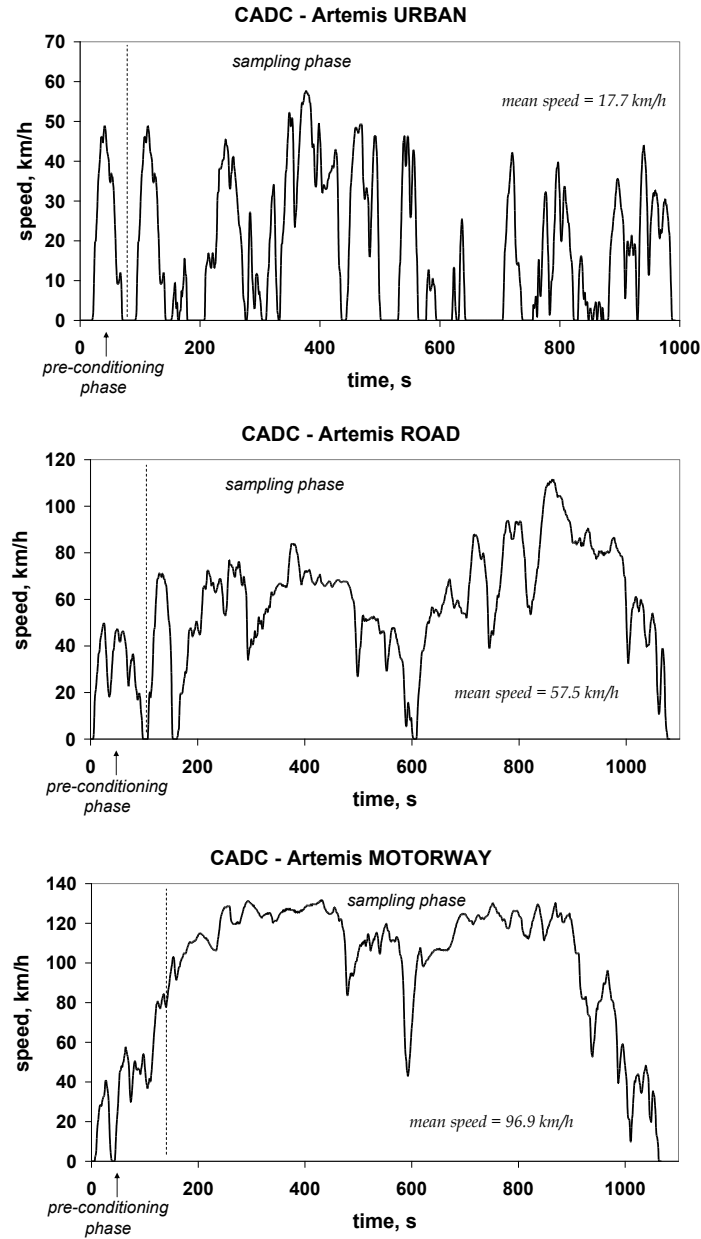


Figure 9. Speed traces of Artemis Urban, Rural and Motorway

The two experimental campaigns are substantially different, not only for the season, but because the first one was “spatial” in the sense that measurements were performed in several sites of Napoli, whereas the second one was “temporal” because it was realized in the same sampling site in Napoli.

This aspect implies that the sampling times of each species during the two campaigns are different; in particular, those relative to spatial campaigns are shorter than those of temporal campaign.

In this section experimental set-up used for ambient air monitoring and the sampling sites of Napoli will be detailed.

3.2.1 The experience of the mobile laboratory

Ambient air measurements were carried out by using a home-made mobile laboratory (Figure 10), equipped with several instruments for measuring pollutant concentrations. The mobile laboratories used during the two experimental campaigns (winter and spring) differ for electrical power supply. During the winter campaign, the mobile laboratory was self-powered by a couple of batteries (12V) connected to an inverter able to supply the needed AC voltage. During the spring campaign, the sampling point was, instead, unchanged making possible to take the power by the fixed electric network, available through the aid of the Comune of Napoli technical service. In this section the experimental set-up is detailed.

The mobile laboratory was equipped with the following instrumentations:

- Video camera for characterising the traffic in terms of numbers per hour of passenger cars, light-duty vehicles, buses and two wheelers;
- Ultrasonic Anemometer (Delta Ohm) for measuring the wind intensity and direction, ambient pressure, temperature and humidity; the sensor of the anemometer was positioned at a height of 2.5 m from the road surface;
- Sampling pump (Bravo Plus) connected with a PM filter holder for measuring total particulate concentration in air; the filter used for air monitoring are borosilicate microfibers reinforced with woven glass cloth and bonded with PTFE characterised by an high aerosol retention (99.9% - Emfab Filter, Pall TX40); the sampling flow rate was 50 lpm; sampling height of 2.5 m from the road surface;
- ELPI by Dekati for particle number concentration and size distribution of particles between 7nm up to 10 µm; sampling height of 2.5 m from the road surface;
- CO analyser for measuring carbon monoxide concentration in ambient air; sampling height of 2.5 m from the road surface;
- Low flow sampling pump connected with active sorbent tube for BTEX sampling (US-EPA, 1999a); the sorbent tubes were the Tenax-TA; the flow rate was of almost 500 ml/min; the sampling time was 15 min or 30 min.



Figure 10 – Some views of the mobile laboratory

Organic compounds (BTEX) collected by sorbent tubes are thermally extracted by using an EDU-GC thermal desorption unit which operates at almost 250°C under helium flow; the desorption unit outlet is connected to the inlet of a Gas-Chromatograph with Flame Ionization Detector (GC_FID); the extracted compounds are automatically injected to GC-FID for the chemical analysis. Figure 11 reports the scheme of VOCs desorption and analysis stages. The calibration of GC-FID was carried out by adsorbing 5 different loads of a certified standard mixture on fresh sorbent tubes. The load of the standard on the sorbent tube was changed by setting a different sampling time in the thermal desorption unit, able to collect the standard from an external inlet (“sampler” in the Figure).

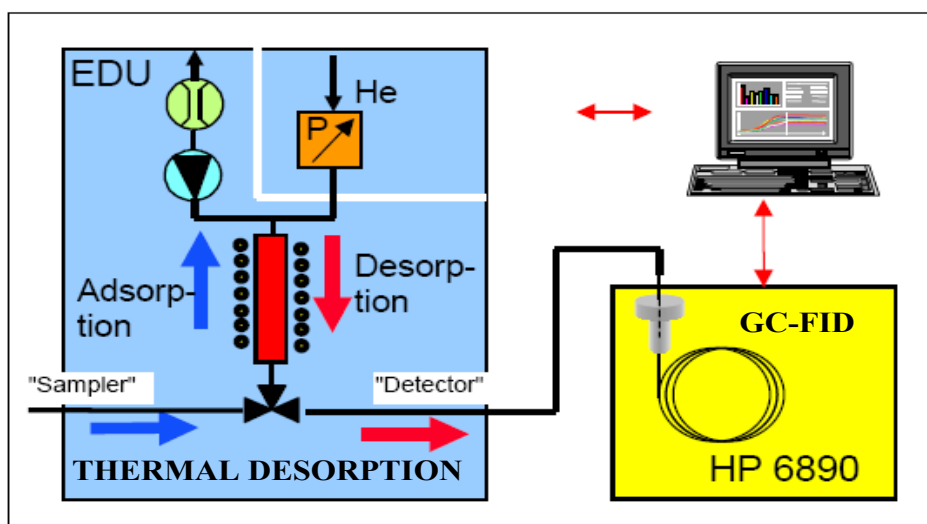


Figure 11. VOCs sampling and analysis set-up

As done for exhaust analysis, the content of PAHs was measured in the PM and PN filters. The analytical method for this computation was described in the previous section 3.1.1.

3.2.2 The sampling sites in Napoli

As already reported above, a first air monitoring experimental campaign was carried out in order to evaluate air quality in different sampling sites in Napoli. The Table 4 details the 7 sites.

Among these there are two urban tunnels (T1 and T2), three urban (UT1, UT2 and UT3) and two sub-urban sites (S-UT and S-UB). The site was classified as urban and sub-urban by following the grouping of air quality monitoring network of Napoli (ARPAC, 2008). Some of the sampling sites are, in fact, close to the air monitoring stations as indicated in Table 4. The urban stations are located in areas with high pollutants concentration gradients, whereas sub-urban ones are located in discontinuous urban areas, generally countries bordering the city centre (S-UT). The sub-urban site of Osservatorio Astronomico is classified as background because it is used for monitoring pollution due to transport phenomena from outside the city. For this reason it is not directly exposed to pollution source but is located in a park.

The Figure 12 shows a map of all the sampling sites and official air quality monitoring stations; S-UT and the close NA09 are located almost 2,5 km outside of the map in the indicated direction.

| SITE | | CLOSE AIR QUALITY MONITORING STATIONS |
|-------------|--------------------------|---------------------------------------|
| T1 | Tunnel delle 4 Giornate | - |
| T2 | Tunnel Chiatamone | - |
| UT1 | Museo | Urban Traffic station - NA06 |
| UT2 | Via S. Teresa | - |
| UT3 | P.zza Garibaldi | Urban Traffic station - NA07 |
| S-UT | Via Argine | Sub-Urban Traffic station - NA09 |
| S-UB | Osservatorio Astronomico | Sub-Urban Background station - NA01 |

Table 4. Sampling sites in Napoli

A second campaign, instead, was realized in the same sampling site UT2 (Via Santa Teresa degli Scalzi) in order to study the temporal variation of air pollution. This road is characterized by an

high traffic volume and classified as a “street-canyon” for the presence of tall buildings on both road sides. This sampling site is positioned near the NA06 air monitoring station (Figure 12).

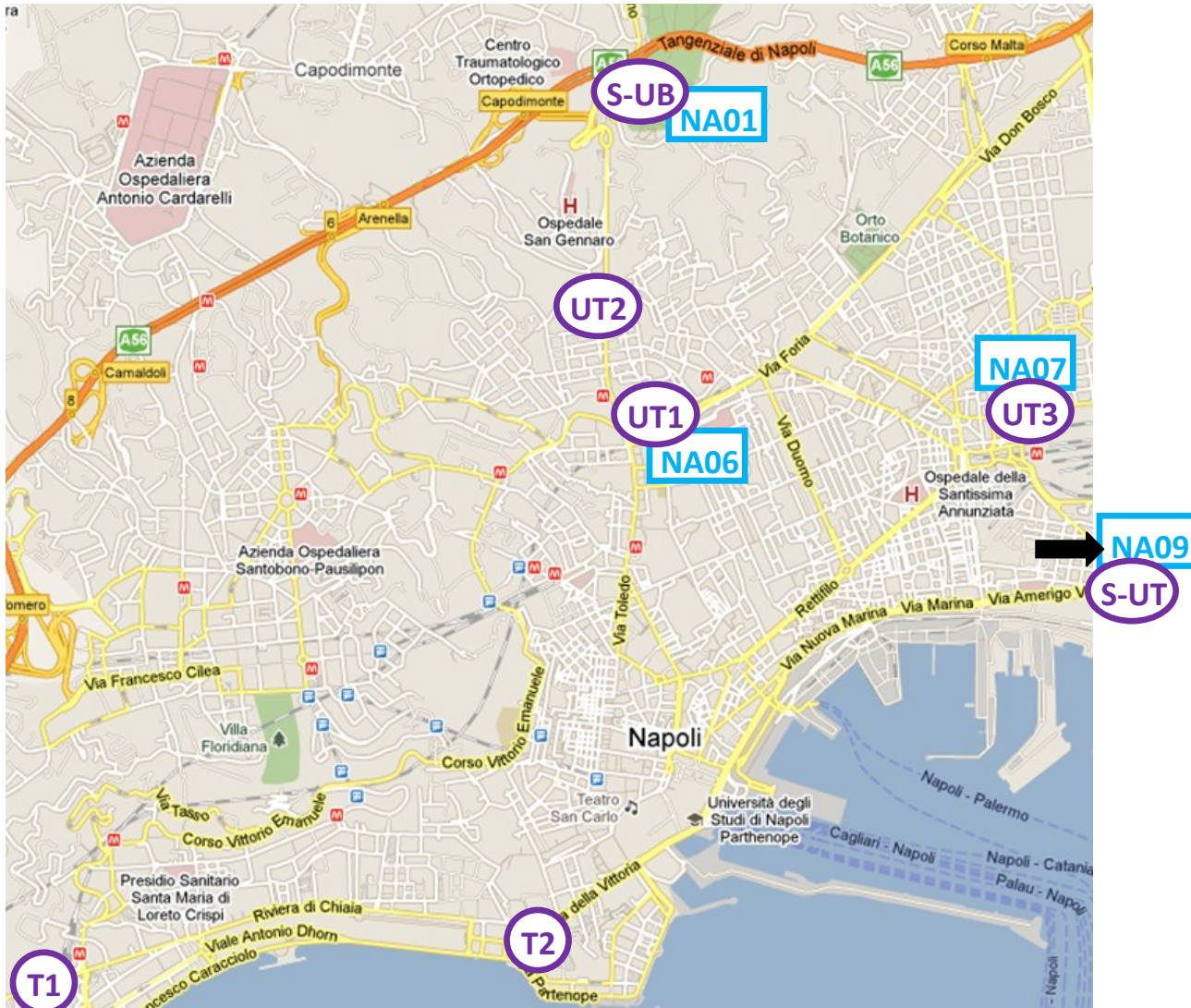


Figure 12. A view of sampling sites

Chapter 4

RESULTS AND DISCUSSION

This section is focused on the description and discussion of the results obtained during the experimental work. First of all, the physical and chemical characterization of the exhaust particulate emissions will be presented in the section 4.1; the section 4.2 is aimed to present the ambient air results of the particulate, the particle phase bounded-PAHs and the BTEXs. The section 4.3 is dedicated to the study of the correlation between the pollution source (vehicle exhaust) and the final effect in urban environment (ambient air concentrations) in the road tunnel environment. The correlation was carried out for BTEXs, PAHs and particle number. As it will be demonstrated in the following, the road tunnel measurements have been suitable for this purpose, offering a good correlation between the exhaust emissions and the ambient air quality, especially for BTEXs and PAHs. Moreover, regarding the PAHs speciation, in the Section 4.4 some diagnostic ratios will be evaluate in order to find any similarities between the exhaust and the air

4.1 Emission factors at the vehicle exhaust

4.1.1 Physical characterization of exhaust particulate

An extensive experimental campaign was carried out to characterize the particulate emissions of different vehicle technologies.

The tested fleet, detailed in the section 3.1.2, is representative of the real circulating park because of the number and the variety of the included vehicles. It is, in fact, composed by 20 vehicles grouped in 4 categories: mopeds, motorcycle with engine capacity higher than 150 cm³, passenger car (PC), and light-duty vehicles (LDV). Each category was further divided in sub-groups according the most significant technology characteristics. In particular, 4- and 2-stroke mopeds were separately considered, whereas PC were characterized by the fuel type (compression ignition - CI, spark ignition - SI, hybrid electric/gasoline and natural gas (NG)). Moreover, the diesel motorizations (CI-PC and LDV) were further separated to take into account the presence of DPF.

All the vehicles were tested over the type-approval legislative driving cycle in order to verify the compliance with emission standards of regulated pollutants. During these tests, particle emissions were also measured. Results are summarized in Table 5. The Table reports the PN and PM emissions (expressed as particles/km and mg/km, respectively) for all the 20 vehicles during the relative type-approval driving cycles. The values correspond to the mean value of three or more repetitions. The variability of the data is explained by the standard deviation, reported next to the mean value.

Data are also displayed in Figure 13 and Figure 14 for better underlining the emission difference due to vehicle category and technologies. The graphs, in fact, do not report the emission data of the single vehicles but the results are grouped according to the vehicle technologies. Bars represent the standard deviation of grouped values. Figures also report the actual Euro 5 standard limit for PM and the future Euro 5b standard limit for PN (5 mg/km and 6×10^{11} particles/km, respectively).

Diesel vehicles still represent the most PM emissive motorization (Figure 13). Diesel passenger cars and light duty vehicles, in fact, emit between 42 and 55 mg/km of PM which correspond to the highest measured values for this pollutant. The emission factors will greatly cut down when a DPF is mounted at the exhaust. When comparing the same vehicle category with and without the DPF, the percentage of reduction of PM emissions is almost 93 %. The presence of the DPF allows to the diesel vehicles to comply with the actual Euro 5 standard limit. PM emission factor is, in fact, almost 3 mg/km and so lower than the limit of 5 mg/km. The PM emissions of the DPF equipped diesel vehicles are comparable with those of the SI passenger cars, whose engine technology coupled with the indirect fuel injection is considered “clean” for particulate production and emissions. For this last category, the PM emissions are, in fact, almost 2 mg/km.

This experimental tests have confirmed that the mopeds category plays a significant role in the particulate urban air pollution. Their emissions are, in fact, very close to those of the diesel vehicles not equipped with DPF, and much higher than the minimum values relative to SI and CI with DPF vehicles. The 2-stroke technology is more polluting than the 4-stroke one. PM of 2-stroke is almost 35 mg/km, that of 4-S is almost 20 mg/km; in other words the PM emissions of 2-stroke mopeds is almost 45% higher than that of 4-stroke. These values agree with Adam et al., 2010. 2-stroke technology is more emissive than 4-stroke one because of the higher content of lubricating oil which takes place to the combustion process. Moreover, the 2-stroke combustion cycle presents the serious disadvantages of the contemporary opening of inlet and outlet valves which allows that part

of the fresh unburned fuel is expelled with the exhaust (scavenging process), increasing the hydrocarbon exhaust emissions. For this reason, the particulate is characterized by an high percentage of organic fraction (Rijkeboer et al., 2005, Czerwinski et al., 2006).

| CATEGORY | TECHNOLOGY | VEHICLE | PARTICLE NUMBER PN, 1/km | | PARTICULATE MATTER, mg/km | |
|-------------------|-------------|-------------------|-----------------------------|---------|------------------------------|---------|
| | | | MEAN | STD DEV | MEAN | STD DEV |
| MOPEDS | 4-S | VESPA PIAGGIO | 5,3E+12 | 6,9E+11 | 3,16 | 2,07 |
| | | HONDA ZOOMER | 9,3E+12 | 1,5E+12 | 13,68 | 4,46 |
| | | PIAGGIO LIBERTY | 1,4E+13 | 1,8E+12 | 22,29 | 12,09 |
| | | PIAGGIO ZIP | 7,1E+12 | 8,6E+11 | 36,06 | 2,19 |
| | 2-S | KIMCO DYNK | 2,2E+13 | 5,4E+11 | 34,54 | 7,20 |
| | | MALAGUTI CIAK | 3,9E+13 | 2,0E+12 | 35,63 | 1,17 |
| MOTORCYCLE >150CC | 4-S | MV AGUSTA BRUTALE | 1,2E+13 | | | |
| PC | CI WITH DPF | NISSAN QUASHQUAI | 2,6E+10 | 1,6E+10 | 4,50 | 3,10 |
| | | ALFA MITO | 6,6E+10 | 3,9E+10 | 2,51 | 1,15 |
| | CI W/O DPF | FIAT 500 | 1,0E+14 | 1,3E+13 | 45,11 | 12,77 |
| | | FIAT ULYSSE | 1,3E+14 | | 68,21 | 5,52 |
| | | FORD MONDEO | 1,3E+14 | | 50,53 | 5,28 |
| | HYBRID | HONDA CIVIC | 1,0E+12 | 3,0E+11 | | |
| | NG | FIAT PUNTO | 5,8E+11 | 1,7E+11 | | |
| | SI | FIAT PUNTO | 1,2E+12 | 2,4E+11 | 1,88 | 0,49 |
| | | RENAULT MEGANE | 2,3E+12 | | | |
| | LDVs | CI W/O DPF | CHRYSLER VOYAGER | 1,2E+14 | 1,4E+13 | 24,09 |
| FIAT DUCATO | | | 2,3E+14 | 3,3E+13 | 60,00 | 8,55 |
| CI WITH DPF | | MERCEDES SPRINTER | 2,1E+11 | 9,1E+10 | 2,15 | 0,48 |
| | | IVECO DAILY | 2,6E+12 | 4,4E+11 | 4,07 | |

Table 5. PM and PN emissions during type approval legislative driving cycles

The Figure 14 reports the same analysis regarding the PN emissions. The graph is semi logarithmic to allow a better representation because of the large difference between the minimum and maximum mean value (almost four orders of magnitude). Before analyzing the data, it has to be pointed that the PN measurement at the vehicle exhaust was realized not following the PMP legislative procedure. A low pressure inertial impactor was used instead of the particle counter and the requested removal of volatiles was not operated. In other words, the measurement of particle

number was realized on the “wet” current and the particles counted are not only the solid particles, but all the particles with the aerodynamic diameter between 7 nm up to 10 μm . A recent study has demonstrated that the volatile particle remover greatly change the particle size distribution and number. It could completely delete the nucleation mode and remove almost 50-90% of the volatiles and sulfates in the accumulation mode (Giechaskiel et al., 2010). The comparison with Euro 5b standard is, indeed, not fully appropriate and it should be interpreted as indicative of the emission level of each vehicle respect to the standard limit.

As for PM emissions, the highest PN emissions (almost 10^{14} particle/km) are produced by CI vehicles (both passenger cars and light-duty).

This maximum value is followed by those relative to the two-wheelers (between 9×10^{12} and 3×10^{13} particle/km). Inside the two wheelers category, the 2-stroke (2-S) mopeds present the highest emissions. The comparison between the 2-stroke and 4-stroke technology states that PN emitted by the former technology is almost 70% higher than that emitted by the latter one.

As result, the two wheelers and the CI vehicles not equipped with DPF have demonstrated to have high emissions not only of particulate mass but also of particle number. Their PN emissions are much higher than Euro5b standard limit.

It is evident that the CI vehicles equipped with DPF greatly reduce the PN emissions, reaching or becoming lower than the standard limit. The CI passenger cars with DPF, in fact, have PN emission of 5×10^{10} particles/km, which is one order of magnitude lower than the limit. The mean PN emissions relative to the LDVs equipped with DPF results instead higher than the limit and characterized by an high standard deviation. This behavior is probably explained by the presence in the same category of two very different vehicles. Despite both vehicles were equipped with a DPF, the engine control of Mercedes Sprinter was designed to work with the DPF at the exhaust; the Iveco Daily with DPF, instead, is an upgrade of the old version of the same vehicle without DPF. Moreover, a high efficiency DPF with a very low porosity is not requested by this vehicle model because its type approval stage (Euro 4) does not impose any PN limit. For this reason, particulate emissions of Mercedes were much lower than those of Iveco Daily (Table 5).

Between the SI vehicles, that which is fuelled with natural gas presents the lowest mean emission value of almost 6×10^{11} . This value is very close to the Euro 5b limit. The hybrid technology of

tested vehicle shows particle emissions of the same order of magnitude of conventional gasoline ones (10^{12} particles/km).

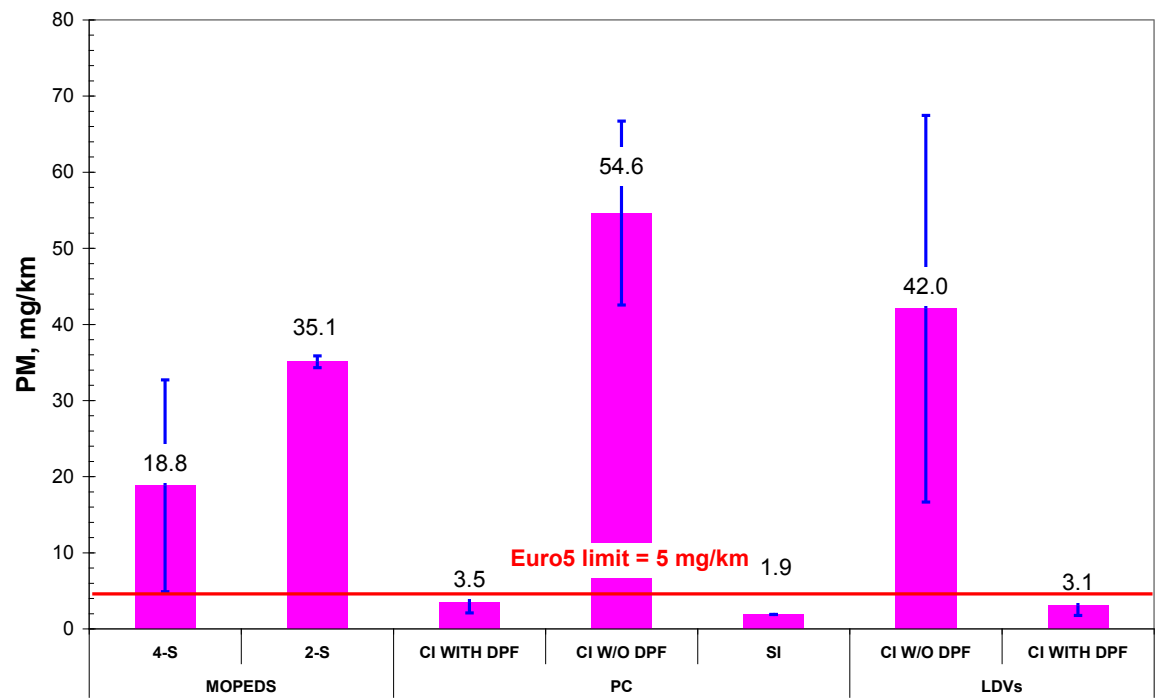


Figure 13. PM emissions during type-approval driving cycles

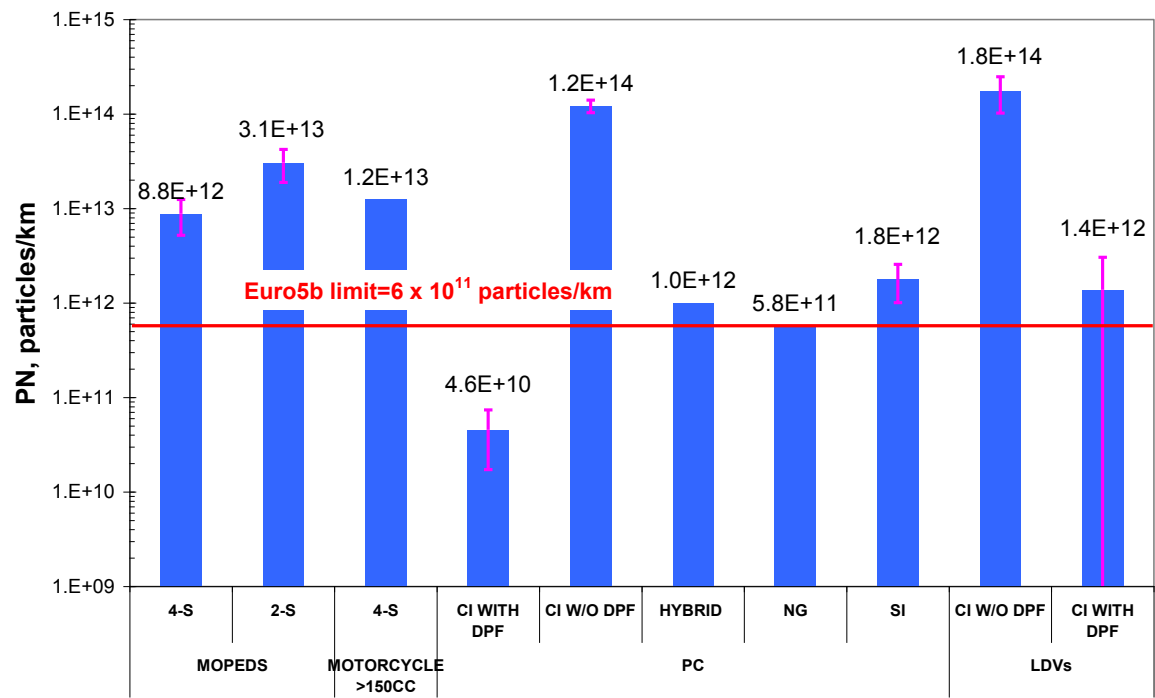


Figure 14. PN emissions during type approval legislative driving cycle

Figure 15 displays the correlation between the PM and PN emissions. For a better visualization, the graph is semi-logarithmic. The plot highlights the emission zones of the different vehicle technologies, summarizing the observations above made.

Starting from high PN and PM values, CI vehicles not equipped with DPF are positioned above 10^{14} particles/km and 20 mg/km; 2-stroke mopeds between 10^{13} - 10^{14} particles/km and above 30 mg/km; 4-stroke motorcycles at almost 10^{13} particles/km and between 2-40 mg/km; CI vehicles with DPF together with SI ones below 3×10^{12} particles/km and 5 mg/km.

It has to be noted that below almost 10^{12} particles/km, measured at the exhaust of SI and CI DPF equipped vehicles, the PM values do not linearly decrease; it remains almost constant around 2-5 mg/km. This value probably corresponds to the detection limit of the procedure for PM measurement. The most critical parameter of the PM measurement at the exhaust of a very low emitter vehicle is the mass collected on the filter. In some cases it is very low, introducing a great error in the measurement. To overcome this problem the new PMP procedure suggests to use a single sampling filter for the whole duration of the driving cycles, and the retention efficiency of the filter should be at least 99%.

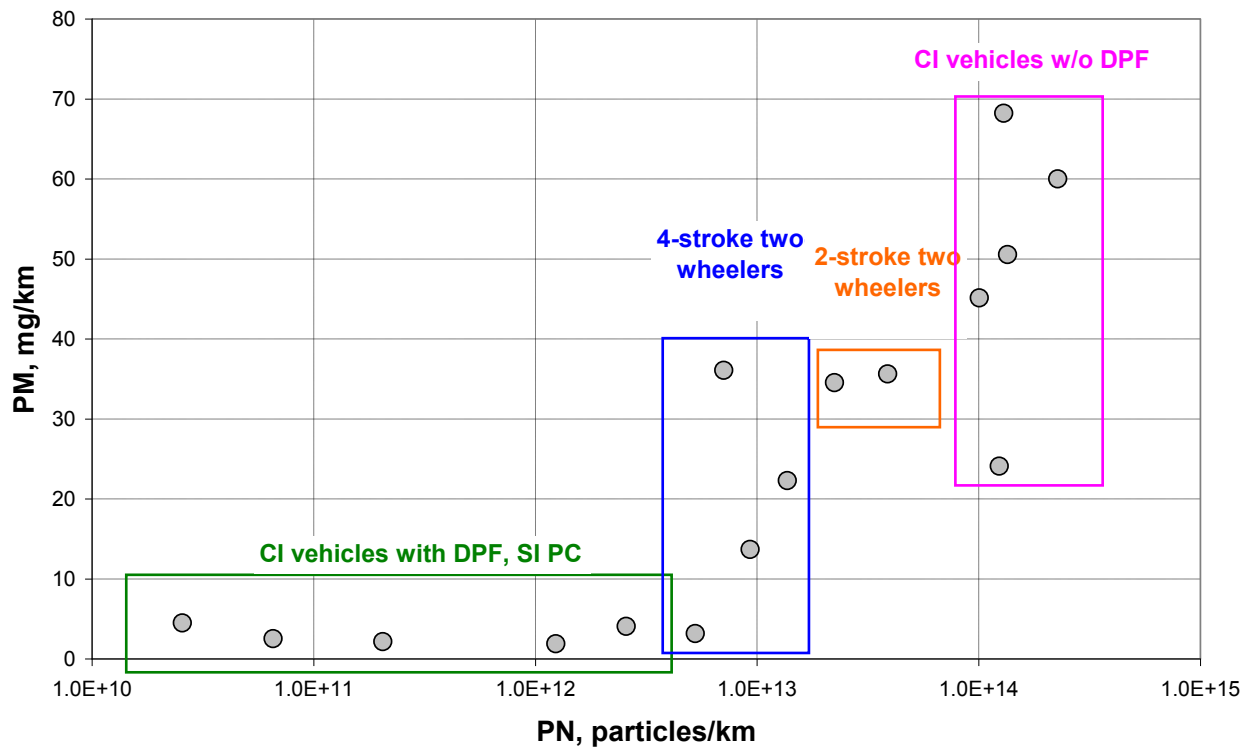


Figure 15. PM vs PN correlation

A series of additional driving cycles (DC) was carried out in order to investigate the influence of driving patterns on particle emissions of each vehicle. For this purpose instantaneous particle emissions were measured during the execution of so called “real” driving cycle, characterized by a higher number of acceleration and deceleration compared to the legislative DC. The kinematic analysis was realized by considering the PN emissions as a function of average speed of driving cycles. This approach is usual in the emission models used to provide an emission inventory. Although it was demonstrated in literature (Rapone et al., 2008) that other kinematic parameters (such as time in acceleration, product of acceleration and speed, time in cruise) influence the emission behavior of the vehicle, the average speed approach is still widely used for its simplicity. The most famous model which uses the average speed as input data for emission computing is the COPERT-COMputer Programme to calculate Emissions from Road Traffic (COPERT 4, 2010).

The complete list of tested legislative and real tested driving cycles is reported in Table 6 which shows the average speed and a brief description in correspondence of each driving cycle. Besides the legislative DC, five real driving cycle were realized (Artemis DC). The detailed description of the DC was given in 3.1.3. As indicated in the table, each cycle was not executed on all the vehicles. For this reason the number of samples referred to the same vehicle is not the same.

For analyzing only the effect of the driving cycle kinematics, modal analysis of particle number emissions was firstly realized on hot results. In this way, the effect due to cold start over-emissions was deleted. Speed dependency of particle emissions is presented in Figure 16 for two-wheelers and in Figure 17 for four-wheelers.

Mopeds produce the highest particle emission during the lowest average speed driving cycles. In fact, both 2- and 4-stroke mopeds have the highest emissions during the real driving cycle Artemis Urban which is characterized by the lowest average speed. Despite the difference of speed with legislative cycle UDC is only 1.2 km/h, the PN emissions are fully different. The PN emissions during Artemis Urban are, in fact, almost 40% higher than those relative to UDC. This observation confirms the thesis that the average speed is a DC parameter not-sufficient to describe the exhaust emission behavior and that, instead, the whole kinematic of a driving cycle influences the emission of a vehicle.

The tested motorcycle has showed an opposite behavior with average speed respect on that observed for mopeds. In particular, the trend of particle emission is strictly increasing with the average speed. The emissions measured during the DC with the highest speed differ of almost 2

order of magnitude respect to those measured during low speed DC. This high emission value is due to the particular operating conditions of motorcycle engine during the high speed DC. When the speed exceeds 120 km/h, the air/fuel engine control is deactivated (open-loop control strategy) and the emissions suddenly increase.

| | Average speed, km/h | Description |
|---|--------------------------------|--|
| Urban Driving Cycle (UDC) | 18,7 | Urban part of legislative DC for PC, LDVs and motorcycle |
| Extra Urban Driving Cycle (EUDC) | 62,6 | Extra-Urban part of legislative DC for PC, LDVs and motorcycle |
| ECEr47 | 24,1 | Legislative DC for mopeds |
| Artemis Urban | 17,5 | Real DC executed on mopeds, PC and LDV |
| Artemis Road | 60,4 | Real DC executed on PC |
| Artemis Motorway | 116,4 | Real DC executed on PC |
| Artemis Cold Urban | 19,04 | Real DC executed on PC, motorcycle and LDV |
| Artemis Cold Road | 41,1 | Real DC executed on PC, motorcycle |
| WMTC part 1 | 24,1 | Legislative DC for motorcycle |
| WMTC part 2 | 54,4 | Legislative DC for motorcycle |
| WMTC part 3 | 94,5 | Legislative DC for motorcycle |

Table 6. List of legislative and real driving cycles (DC)

Looking at the results of four wheelers, it could be noted that all the considered categories with the exception of diesel passenger cars equipped with DPF show a decreasing emission trend with the average speed of driving cycles. The diesel passenger cars with DPF which present the minimum measured values, instead, have an inverse trend: PN emissions increase of one order of magnitude moving from 20 to 120 km/h.

Additional steady-state tests were performed in order to characterize dimensional distribution of exhaust particulate. Results are showed in Figure 18, Figure 20, Figure 21 and Figure 22 relative to the two-wheelers, the SI passenger cars, the CI passenger cars and the LDV, respectively. The graphs report the number of particles normalized respect to the particle dimensional range ($dN/d\log D_p$), versus the aerodynamic diameter. The graphs start from few nm and are interrupted at 1 μm because the 99% of the exhaust particle number distribution is developed in this dimensional range.

Figure 18 separately groups particle size distribution of 2-stroke mopeds, of 4-stroke ones and of the motorcycle. Particle distribution for mopeds was measured at 20 and 45 km/h, whereas that of the motorcycle was measured in a major number of speeds (30, 50, 70 and 120 km/h). Distribution of 4-S mopeds is different from that of 2-S. Even if they both peak at almost 100 nm, particles at the exhaust of 4-S have a higher contribution of larger particles. This is explained by the presence in the 4-stroke category of a moped without catalyst. The absence of a catalyst, in fact, enhances the agglomeration of particles in the exhaust pipe and so causes the formation of larger particles (Ronkko et al., 2006). Both categories (2- and 4-stroke) present an increasing number of particles when speed increases. Because of the simplified automatic gear, the mopeds, in fact, are forced to work with an increasing load when the speed increases. This aspect leads to a higher emission production when speed and load increase.

For the motorcycle, a bimodal distribution is evident. The first peak (nucleation mode) is positioned at almost 30 nm and the second (accumulation mode) at almost 120 nm. The evidence of nucleation mode is due to the higher contribution of volatiles, mainly constituted by unburned hydrocarbons. They become predominant during high speed test. It was already highlighted that the combustion quality is not controlled over 120 km/h. This open-loop operating condition explains the abnormal presence of hydrocarbons and as consequence the elevated presence of nanoparticles. The extra-emission of particles and hydrocarbons is highlighted in Figure 19 where PN emissions measured during the legislative driving cycle are plotted. It is evident that when moving from 90 to 120 km/h PN increase of almost three orders of magnitude and almost the whole number of particles has a diameter lower than 30 nm. This size distribution is typical of the exhaust enriched in volatiles.

At the exhaust of motorcycle, the trend of particle number with the speed is not monotonous; the highest number of particles, in fact, is measured during the lowest speed test of 30 km/h. This behavior, different from that highlighted for mopeds, is explained by the variety of possible

operating conditions of the vehicle, which is able to work in different engine speed and load combinations depending on the chosen gear ratio.

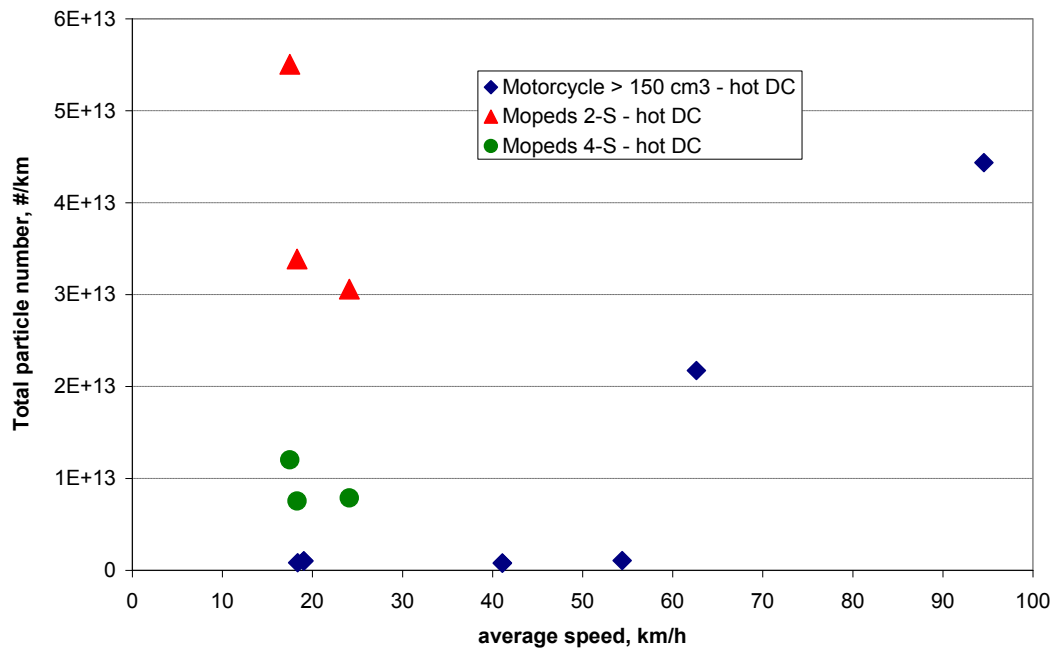


Figure 16. Speed dependency of particle emissions of two-wheelers during hot start driving cycles

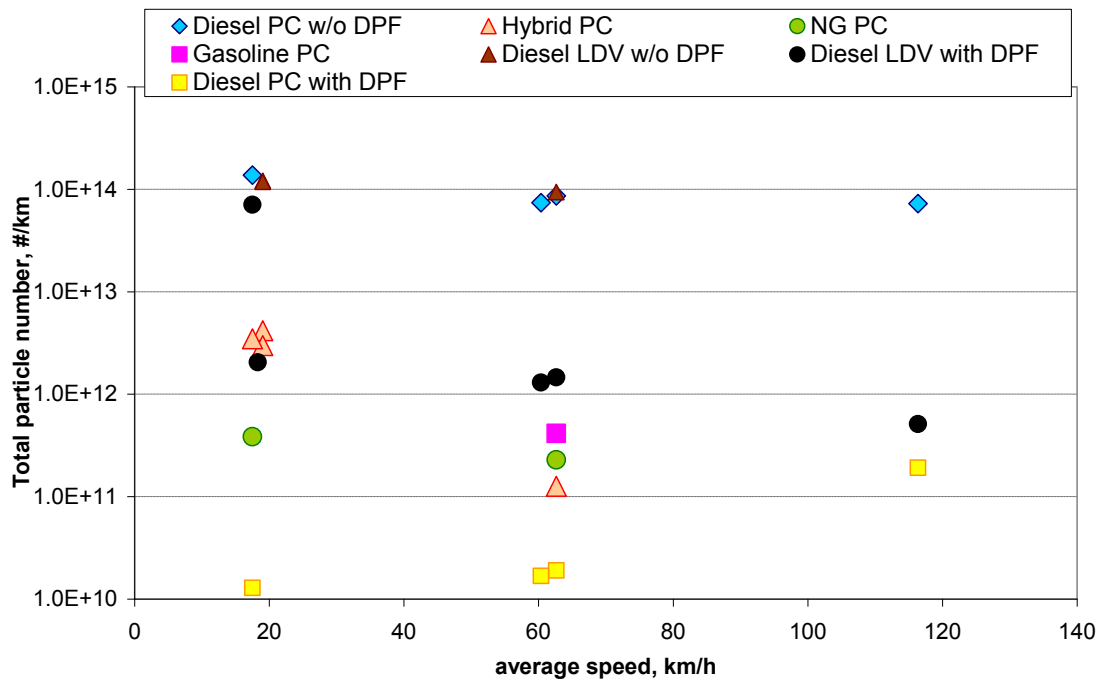


Figure 17. Speed dependency of particle emissions of four-wheelers during hot start driving cycles

Figure 20 summarizes the result of SI passenger cars. The particle size distribution of gasoline and compressed natural gas fuelled cars is bimodal. In this case, peaks are shifted towards lower aerodynamic diameters than those relative to the two-wheelers; a peak is, in fact, clearly positioned

at almost 80 nm. The measured distribution also suggests the presence of a second peak in the region of ultrafine particles with the diameter lower than 7 nm which corresponds to the minimum detectable diameter of the instrumentation used in this experimental work for measuring particle size distribution. Particle size distribution of hybrid passenger car is slightly different. First of all, there is no evidence of a peak in the region of smallest particles. This agrees with the very low content, in some cases not detectable by the gas analyzer, of hydrocarbons at the exhaust of this vehicle. Moreover, besides the main peak is positioned at almost 80 nm like the other examined SI passenger cars, the particle size distribution of hybrid vehicle includes a higher relative percentage of particles larger than 200 nm. In other words, at the exhaust of this vehicle agglomeration process seems to be enhanced. Regarding the dependence on the speed for SI vehicles, it has to be noted that, when increasing the vehicle speed, the particle number tends to decrease. The particle size distribution measured during the 30 km/h constant speed test is, in fact, positioned in the upper part of graphs.

Figure 21 displays the particle size distribution of diesel vehicles. Results of vehicles not equipped with DPF are distinguished by those of vehicles with DPF. The dimensions of particles emitted by diesel vehicles without DPF have a modal distribution with the peak around 80 nm. For this category, the particle emissions increase with the speed. About this, it is interesting to note the different emission behavior of SI and CI vehicles. Figure 23 reports PN emission traces measured at the exhaust of the CI and SI passenger cars during a module of UDC driving cycle. The particle emissions at the exhaust of diesel vehicles not equipped with DPF follow the speed trend: for this motorization the engine load is the main influencing parameter for particulate production. The emissions of SI vehicle are, instead, mainly influenced by the dynamic speed variation occurring during the accelerations, the decelerations and the gear changes. This behavior explains the speed dependence of PN emissions of SI passenger cars: PN is high during the low speed test of 30 km/h because of the major number of acceleration and deceleration caused by the difficulty to maintain the vehicle at this constant speed. When speed increases, the driver is able to maintain more precisely the speed constant avoiding the dynamic operation of the engine.

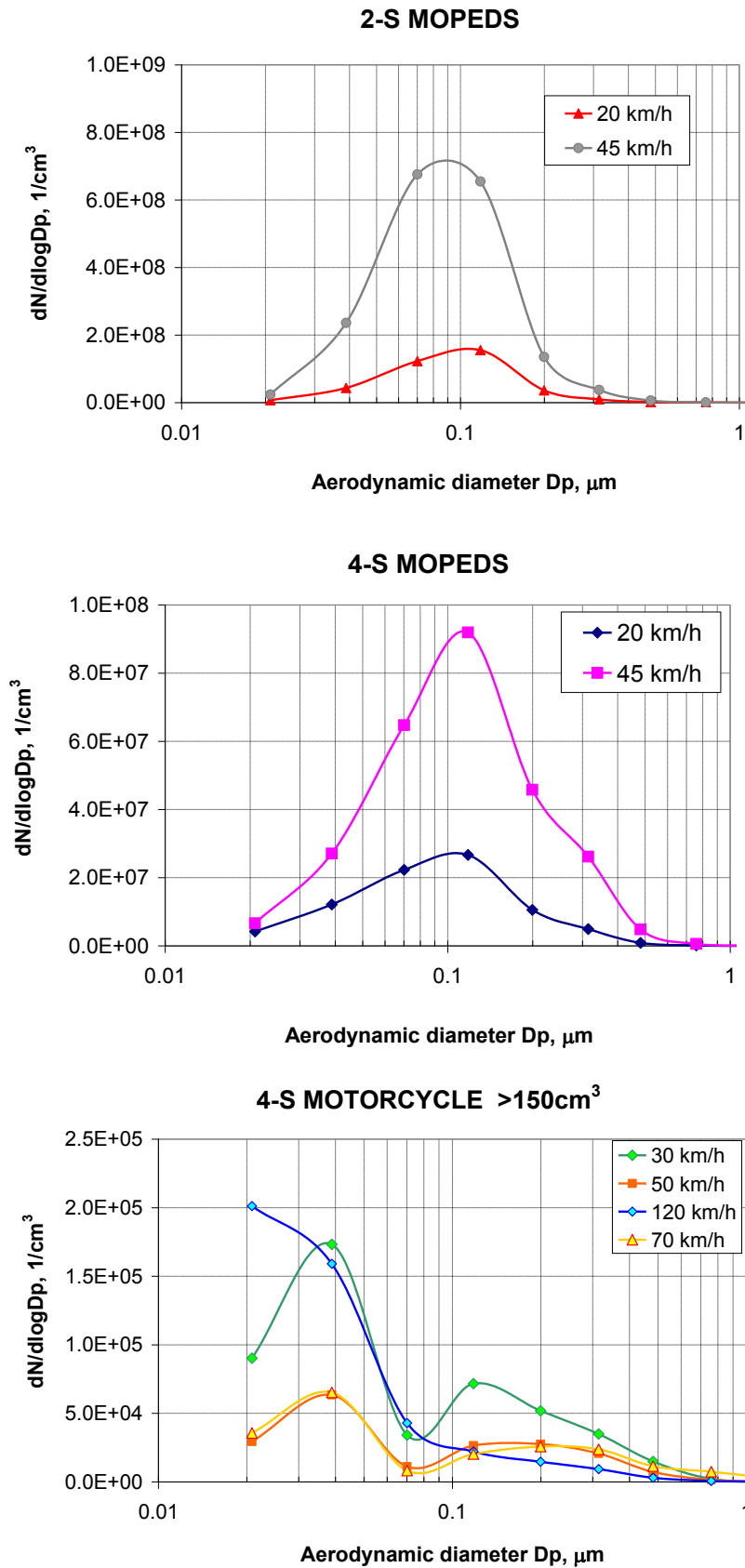


Figure 18. Particle size distribution at the exhaust of two-wheelers

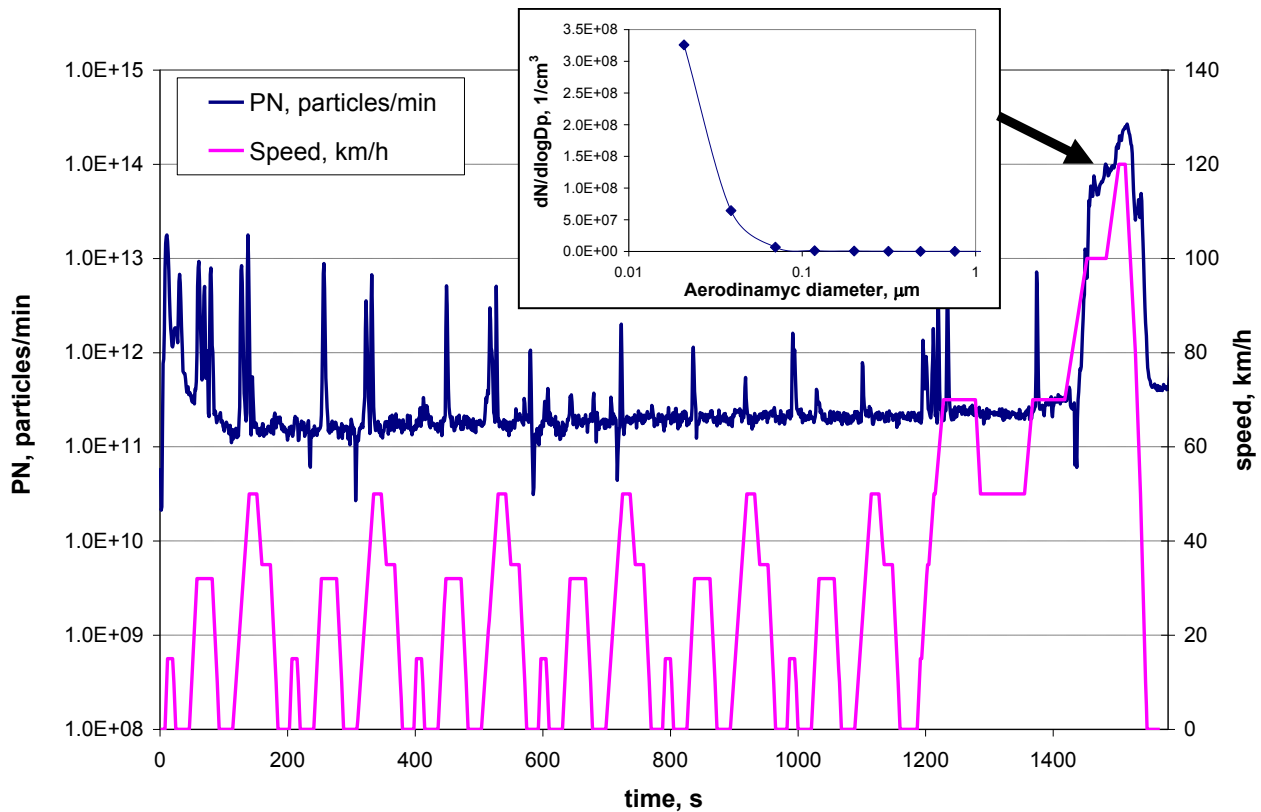


Figure 19. PN emissions of the motorcycle over legislative type approval driving cycle

When looking at the size distribution of diesel DPF-vehicles, it is evident that in most cases a decreasing trend with particle diameter was measured. The smallest particles constitute, in fact, also the most numerous. The distribution slightly changes during 70 and 90 km/h, because of the presence of some emission peaks, not well explained. It has to be pointed that measured values are very low; in the next section it will be possible to note that these numbers are lower than those measured in a clean ambient air. Moreover, they are very close to detection limit of ELPI; this aspect affects the measurements with a larger error.

In the Figure 22 relative to the results of LDV, there are no big differences between the distributions of vehicles with and without DPF, with the exception of values measured which are obviously much high for vehicles without DPF. The inclusion in the same category of LDV with DPF of two very different technologies (a low and a high emitter) modify the mean size distribution, making it more similar to that relative to the same vehicles not equipped with DPF. The size distribution peaks at almost 80 nm, and the contribution of smaller particles varies depending on vehicle speed.

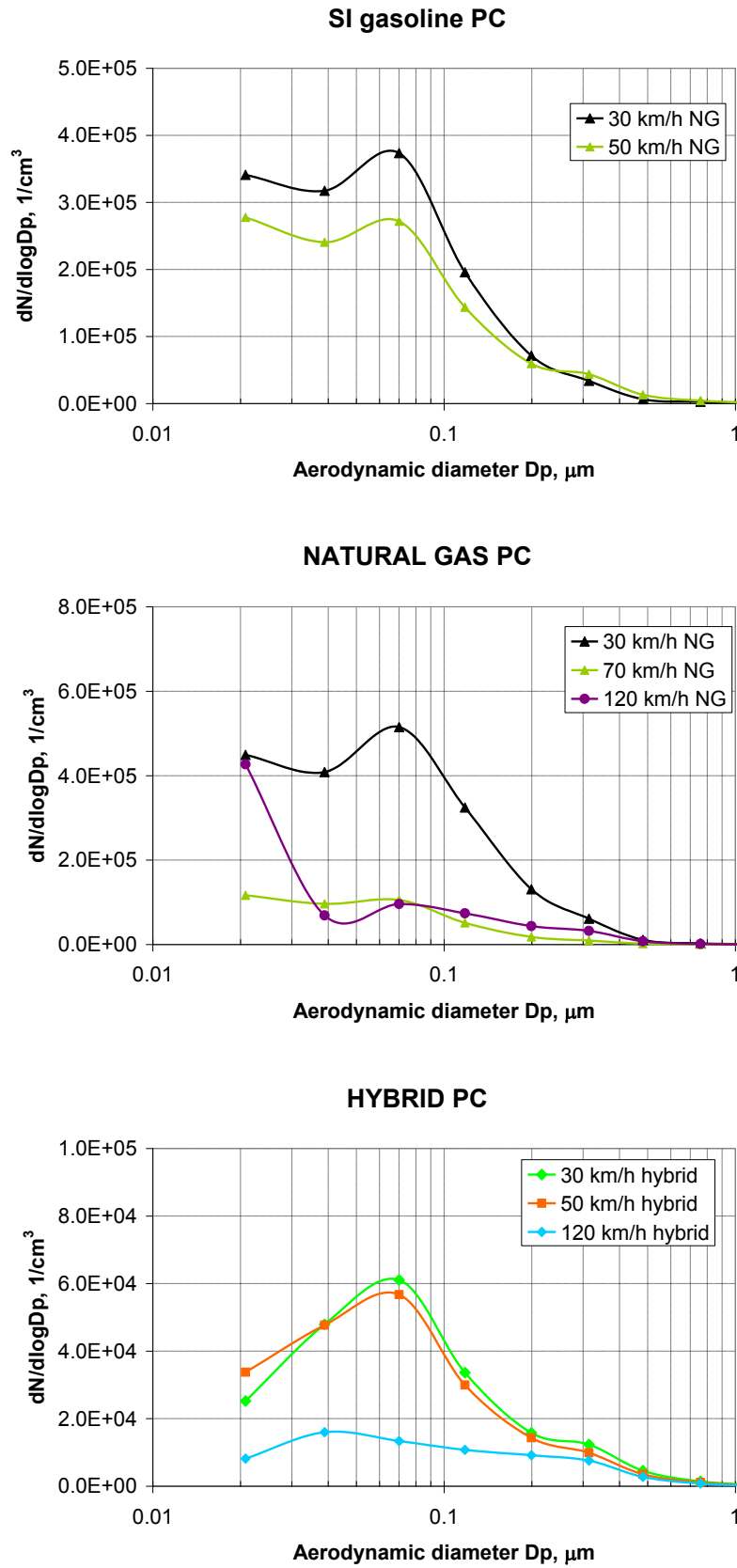


Figure 20. Particle size distribution of SI passenger cars

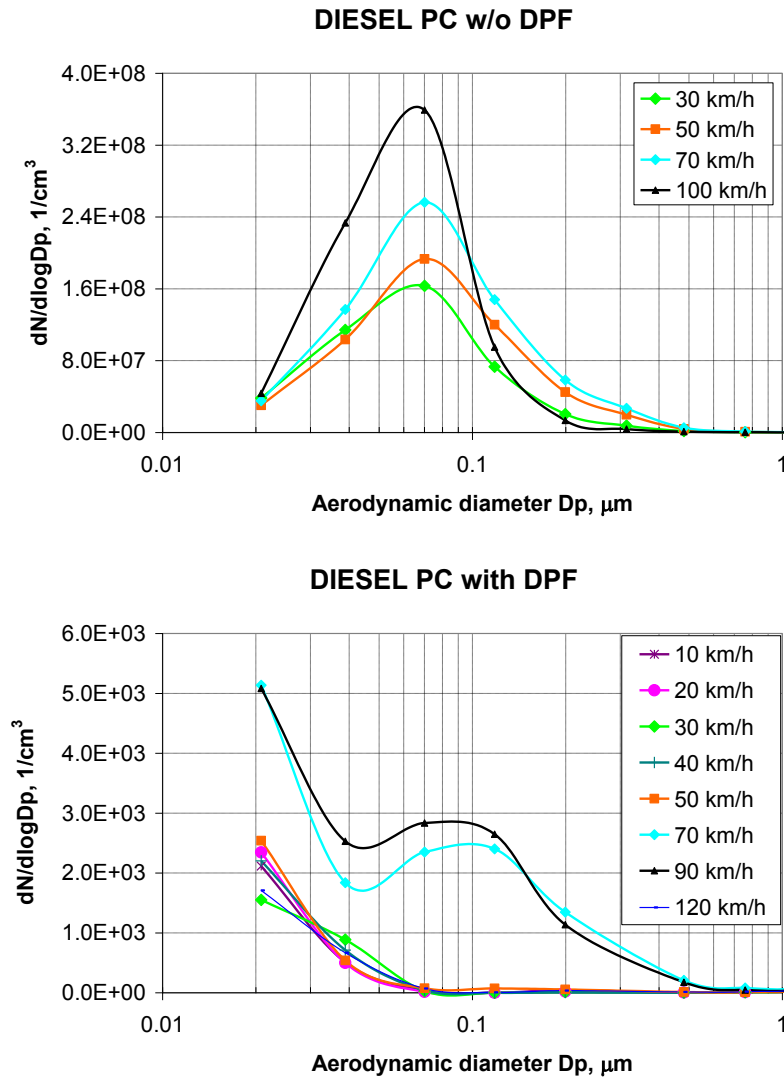


Figure 21. Particle size distribution of CI passenger cars

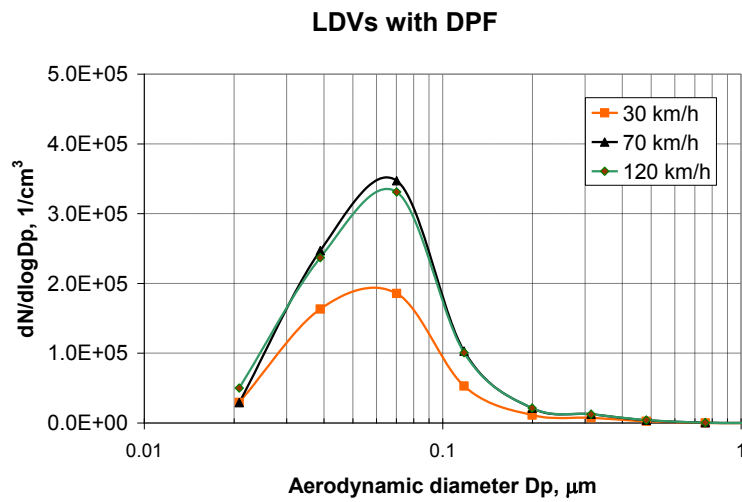
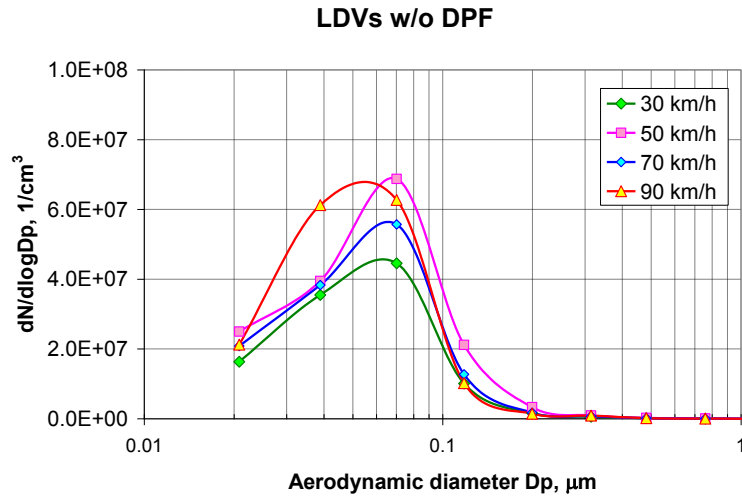


Figure 22. Particle size distribution of LDVs

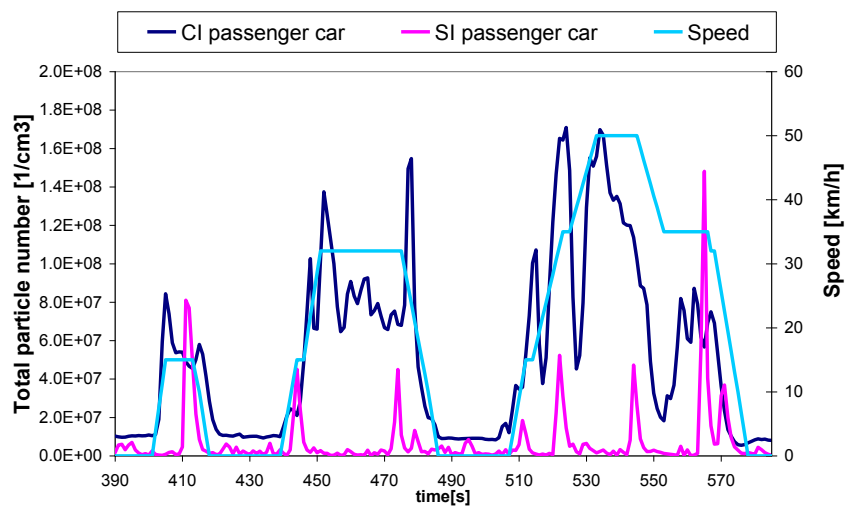


Figure 23 – PN emissions of CI and SI passenger cars during the UDC

4.1.2 Chemical characterization of exhaust particulate – PAHs content

As detailed in the experimental set-up section, a chemical characterization of particulate collected on the ELPI filters was executed for some vehicles of the tested fleet. This analysis was aimed to evaluate the content of Polycyclic Aromatic Hydrocarbons (PAHs) bounded to the particulate.

The vehicles subjected to this analysis were listed in Table 7. There are 2 gasoline two-wheelers and 2 diesel four-wheelers not equipped with DPF.

| VEHICLE | DESCRIPTION |
|---------------------|----------------------------------|
| VESPA PIAGGIO 4T 4V | 4-STROKE MOPED |
| MV AGUSTA BRUTALE | MOTORCYCLE > 150 cm ³ |
| FIAT 500 | CI PC w/o DPF |
| FIAT DUCATO | LDV w/o DPF |

Table 7. Vehicles subjected to the particulate chemical characterisation

Emission factors of the single PAH expressed as $\mu\text{g}/\text{km}$ and measured during the execution of the legislative driving cycles are reported in Table 8. For each vehicle, the table provides emission values of the three examined dimensional groups and for the total quantity extracted by all ELPI filters. As above mentioned, in fact, ELPI filters were grouped in three size classes each composed by four filters, including, respectively, particles with the aerodynamic diameter lower than $0,1 \mu\text{m}$, belonging to $0,1 - 1 \mu\text{m}$ range and higher than $1 \mu\text{m}$. The table provides also the sum of the quantified PAHs and of the compounds defined carcinogenic by the IARC. These last are highlighted in bold.

Total PAHs range between 30 and $50 \mu\text{g}/\text{km}$ for all the vehicles with the exception of the motorcycle whose emissions reach almost $180 \mu\text{g}/\text{km}$. The highest PAHs content in collected particulate is another effect of the extra-emissions occurring during the high speed test of $120 \text{ km}/\text{h}$ performed with this motorcycle (see Figure 19). The open loop engine control strategy actuated at high speed produces a large emission of nanoparticles and unburnt hydrocarbons which also justifies the high PAHs emissions.

| PAH, µg/km | | | | | | | | | | | | | | | | |
|---|----------------|---------|---------|-------|-------------------------------|---------|---------|-------|---------------|---------|---------|-------|-------------|---------|---------|-------|
| | 4-stroke moped | | | | motorcycle>150cm ³ | | | | CI PC w/o DPF | | | | LDV w/o DPF | | | |
| | Group 1 | Group 2 | Group 3 | Total | Group 1 | Group 2 | Group 3 | Total | Group 1 | Group 2 | Group 3 | Total | Group 1 | Group 2 | Group 3 | Total |
| phenanthrene | 2.56 | 1.52 | 0.83 | 4.92 | 21.90 | 28.09 | 4.18 | 54.17 | 8.23 | 3.70 | 1.26 | 13.20 | 4.46 | 1.54 | 3.56 | 9.56 |
| anthracene | 0.77 | 0.35 | 0.14 | 1.26 | 2.45 | 3.33 | 0.48 | 6.26 | 2.24 | 0.80 | 0.16 | 3.21 | 0.30 | 0.16 | 0.32 | 0.79 |
| fluoranthene | 0.8 | 0.8 | 0.7 | 2.3 | 9.9 | 5.9 | 3.4 | 19.2 | 2.4 | 1.4 | 0.7 | 4.5 | 1.6 | 0.6 | 2.3 | 4.5 |
| pyrene | 0.9 | 0.7 | 0.5 | 2.1 | 8.7 | 6.7 | 2.3 | 17.8 | 3.0 | 1.2 | 0.6 | 4.8 | 2.2 | 1.0 | 2.3 | 5.5 |
| 3,4-benzofluorene | 0.0 | 0.0 | 0.0 | 0.0 | 3.4 | 1.6 | 0.3 | 5.4 | 0.4 | 0.1 | 0.2 | 0.7 | 0.8 | 0.2 | 0.4 | 1.3 |
| benzo(a)anthracene | 1.4 | 0.3 | 0.3 | 1.9 | 8.6 | 1.8 | 2.2 | 12.7 | 1.6 | 1.1 | 0.8 | 3.4 | 1.7 | 0.8 | 1.6 | 4.1 |
| chrysene | 1.4 | 0.2 | 0.1 | 1.7 | 4.8 | 1.8 | 1.1 | 7.7 | 1.0 | 0.8 | 0.4 | 2.1 | 0.6 | 0.4 | 0.8 | 1.7 |
| 5-methyl chrysene | 0.4 | 0.2 | 0.0 | 0.6 | 0.0 | 0.0 | 0.0 | 0.0 | 0.7 | 0.0 | 0.0 | 0.7 | 0.2 | 0.0 | 0.0 | 0.2 |
| benzo(b+k)fluoranthene | 3.4 | 0.6 | 0.1 | 4.1 | 5.1 | 2.7 | 1.2 | 9.0 | 2.0 | 0.8 | 0.3 | 3.1 | 1.8 | 1.4 | 1.4 | 4.6 |
| benzo(j)fluoranthene | 1.1 | 0.3 | 0.1 | 1.4 | 3.7 | 2.0 | 1.9 | 7.6 | 1.1 | 1.1 | 0.5 | 2.7 | 0.0 | 0.0 | 0.0 | 0.0 |
| benzo(e)pyrene | 1.2 | 0.4 | 0.3 | 1.9 | 7.1 | 1.2 | 1.5 | 9.9 | 1.1 | 0.5 | 0.1 | 1.6 | 0.5 | 0.4 | 0.4 | 1.3 |
| benzo(a)pyrene | 1.9 | 0.4 | 0.1 | 2.3 | 6.5 | 0.8 | 1.7 | 9.0 | 1.1 | 0.5 | 1.8 | 3.3 | 0.5 | 0.5 | 0.7 | 1.7 |
| perylene | 1.4 | 0.4 | 0.3 | 2.1 | 5.5 | 2.3 | 0.7 | 8.5 | 1.2 | 1.0 | 0.9 | 3.2 | 0.8 | 0.9 | 0.8 | 2.5 |
| indeno(1,2,3,c,d)pyrene | 1.5 | 0.3 | 0.0 | 1.8 | 2.7 | 0.6 | 0.0 | 3.3 | 0.9 | 0.4 | 0.0 | 1.3 | 0.0 | 0.2 | 0.4 | 0.6 |
| dibenzo(a,h)anthracene | 0.4 | 0.0 | 0.0 | 0.4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| benzo(g,h,i)perylene | 0.3 | 0.4 | 0.0 | 0.7 | 2.6 | 0.8 | 0.0 | 3.4 | 1.1 | 0.4 | 0.0 | 1.5 | 0.4 | 0.3 | 0.4 | 1.2 |
| dibenzo(a,e)pyrene | 0.7 | 0.0 | 0.0 | 0.7 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| coronene | 1.1 | 0.2 | 0.0 | 1.3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.7 | 0.2 | 0.0 | 0.8 | 0.0 | 0.3 | 0.0 | 0.3 |
| dibenzo(a,h)pyrene | 0.4 | 0.0 | 0.0 | 0.4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| dibenzo(a,i)pyrene | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| dibenzo(a,l)pyrene | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Total PAH | 21.4 | 7.0 | 3.3 | 31.8 | 93.1 | 59.7 | 21.0 | 173.9 | 28.7 | 13.9 | 7.7 | 50.2 | 15.8 | 8.8 | 15.3 | 39.8 |
| Total carcinogenic PAH | 11.7 | 2.2 | 0.5 | 14.5 | 31.5 | 9.7 | 8.1 | 49.3 | 8.4 | 4.5 | 3.7 | 16.6 | 4.7 | 3.3 | 4.9 | 13.0 |
| Group 1: <0.1 µm; Group 2: 0.1-1 µm; Group 3: >1 µm | | | | | | | | | | | | | | | | |

Table 8. PAHs emission factors

The sum of quantified PAHs is almost 0,5 % of total emitted hydrocarbons for diesel vehicles and almost 0,1 % for gasoline ones. The higher content of polycyclic aromatics (characterised by medium and high molecular weight) in diesel fuel respect to that in the gasoline is reflected also into the exhaust quality.

The distribution of PAHs according to their molecular weight is presented in Figure 24. Low Molecular Weight (LMW) includes compounds from phenanthrene to fluoranthene (3-4 aromatic rings), Middle Molecular Weight (MMW) from pyrene to benzo(b+k+j)fluoranthene (4-5 aromatic rings) and High Molecular weight (HMW) from benzo(e)pyrene to dibenzo(a,l)pyrene (more than 5 aromatic rings). Looking at the results, it seems clear that the sum of low and middle molecular weight PAHs ranges between 60-80% of the total PAHs. The HMW compounds cover the remaining percentage, representing, indeed, the lowest amount. Besides this mean distribution, it is not possible to trace an unique trend for the relative contributions of the several weight PAHs groups to the three dimensional particle groups.

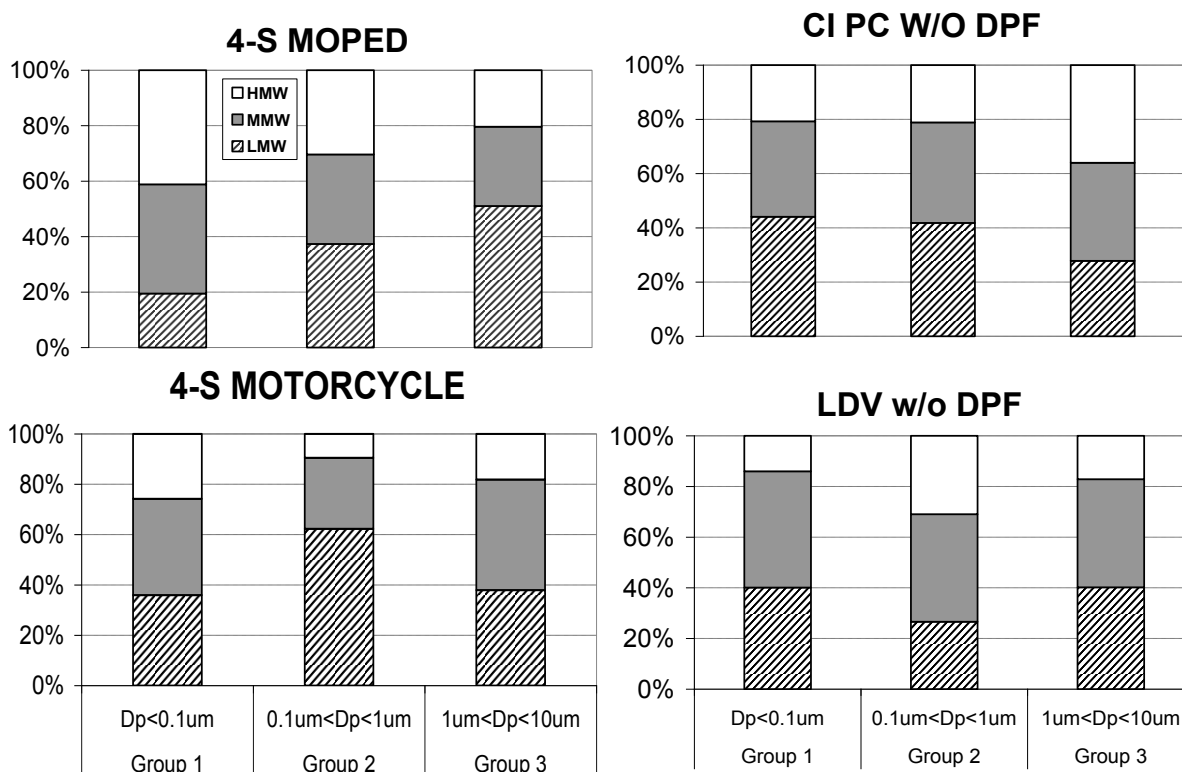


Figure 24. Low Molecular Weight (LMW), Middle Molecular Weight (MMW) and High Molecular Weight (HMW) PAH distribution

Figure 25 compares the sum of the PAHs measured in particle phase (expressed as $\mu\text{g}/\text{km}$) with the total particles measured by ELPI (expressed as $\text{particle}/\text{km}$) in order to evaluate if a correlation exists. Because of the few number of observations, it is very difficult and probably it should be not fully correct, to evaluate a correlation law with an assessment of the error. For this reason a qualitative analysis is presented. The Figures shows that the two quantities are linearly weakly correlated only if the data point relative to the motorcycle is excluded. For the diesel vehicles and the moped an increase of PN emissions is related to an increase of the PAHs content, even if the percentage variations result very different. The data relative to the motorcycle, instead, is positioned quite far from this correlation trend: the PAHs content is higher compared to the particle number. This result is explained by enormous production of volatiles during the high speed period of driving cycle, which greatly influences the PAHs content in particle phase but not the particle number. Because of the negligible duration of the peak during the driving cycle (almost 6% of total duration), the mean particle number emissions during the driving cycle only change of one order of magnitude; this increment is percentage lower than that suffered by PAHs.

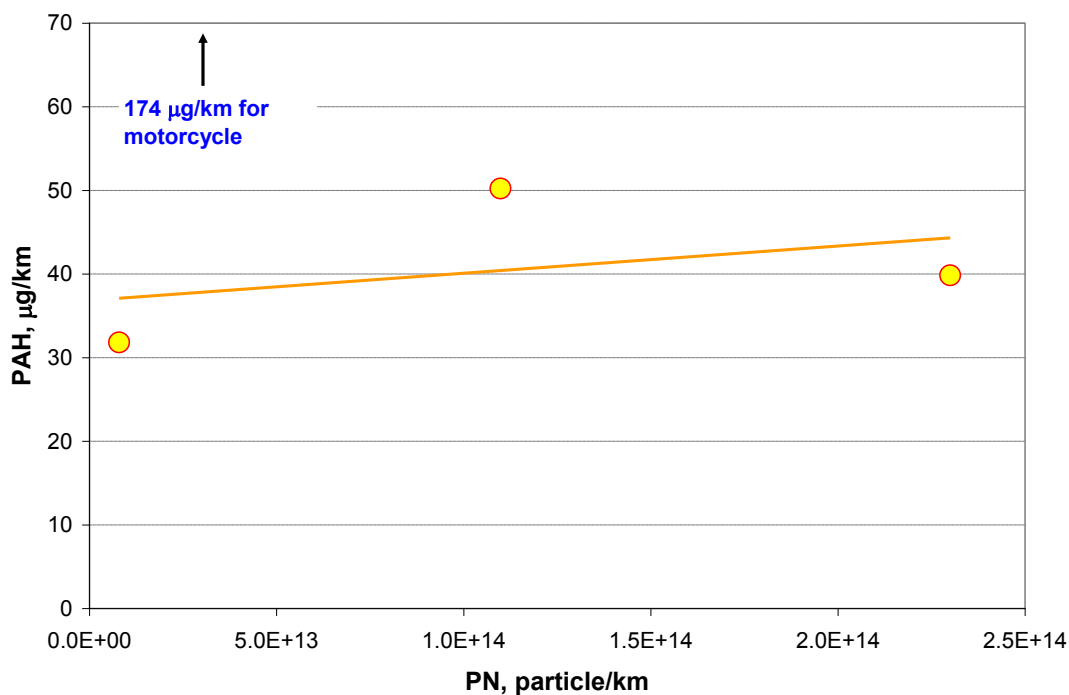


Figure 25. PN and PAH correlation

Results of the sum of PAHs and of carcinogenic benzo(a)pyrene are presented in Figure 26 and Figure 27 as size distribution in a similar manner already made for particle number. Because the three analyzed ELPI groups are not equally distributed in terms of dimensions, the most correct way to present the data is by dividing the absolute quantity for the dimensional range expressed as

logarithmic difference ($dM/d\log D_p$ in the Figures). By analysing the dimensional distribution of total PAHs, a marked reduction of PAHs content is visible when moving from the second to the third size group for all the vehicles with the exception of LDV. In other words, the major contribution of PAHs is given by particle smaller than $1\ \mu\text{m}$ (PM₁) which also corresponds to the dimensional range where the particle number distribution is included. This result agrees with Yang et al., 2005. The LDV vehicle shows, instead, a comparable level of PAHs in all the three size groups.

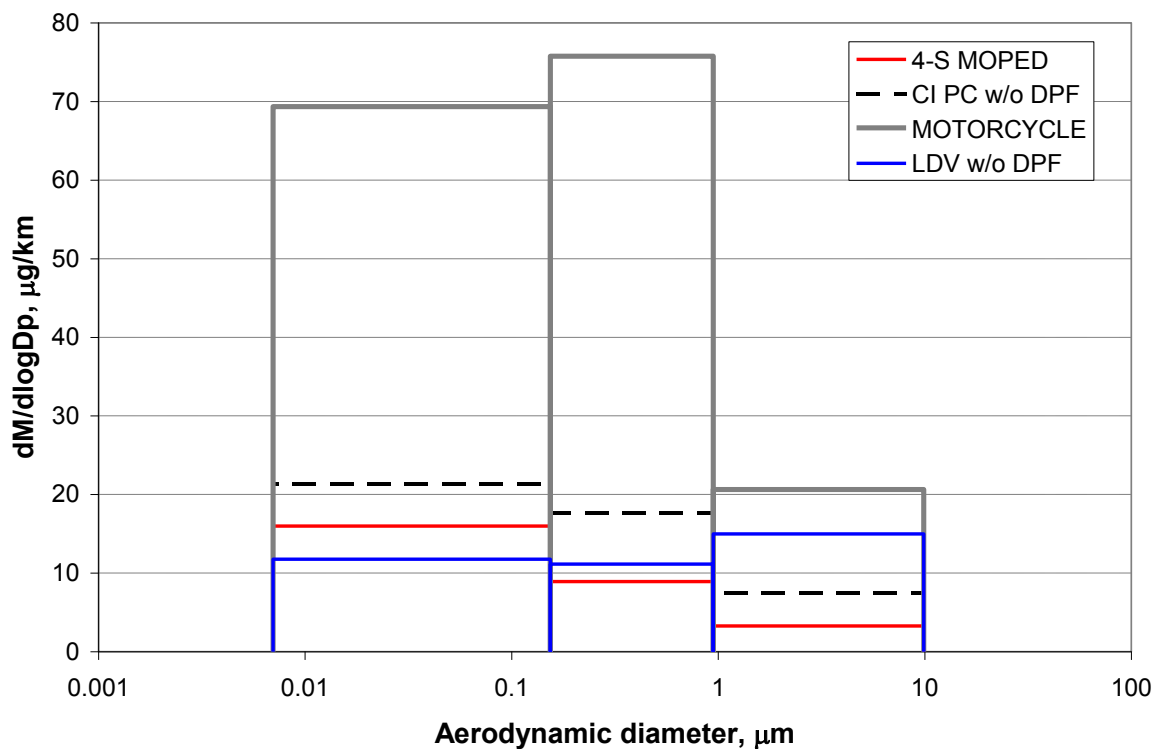


Figure 26. PAHs size distribution

Looking at benzo(a)pyrene, its concentration ranges between 0.5 and $5\ \mu\text{g}/\text{km}$. The size distribution of the two wheelers presents the highest value in the first particle dimensional range (diameter lower than $0.1\ \mu\text{m}$), reflecting what happens for total PAHs. For diesel vehicles, benzo(a)pyrene emissions seem to be not particle size dependent. If variability of the data is considered, measured values in the three size groups are, in fact, comparable (around $1\ \mu\text{g}/\text{km}$).

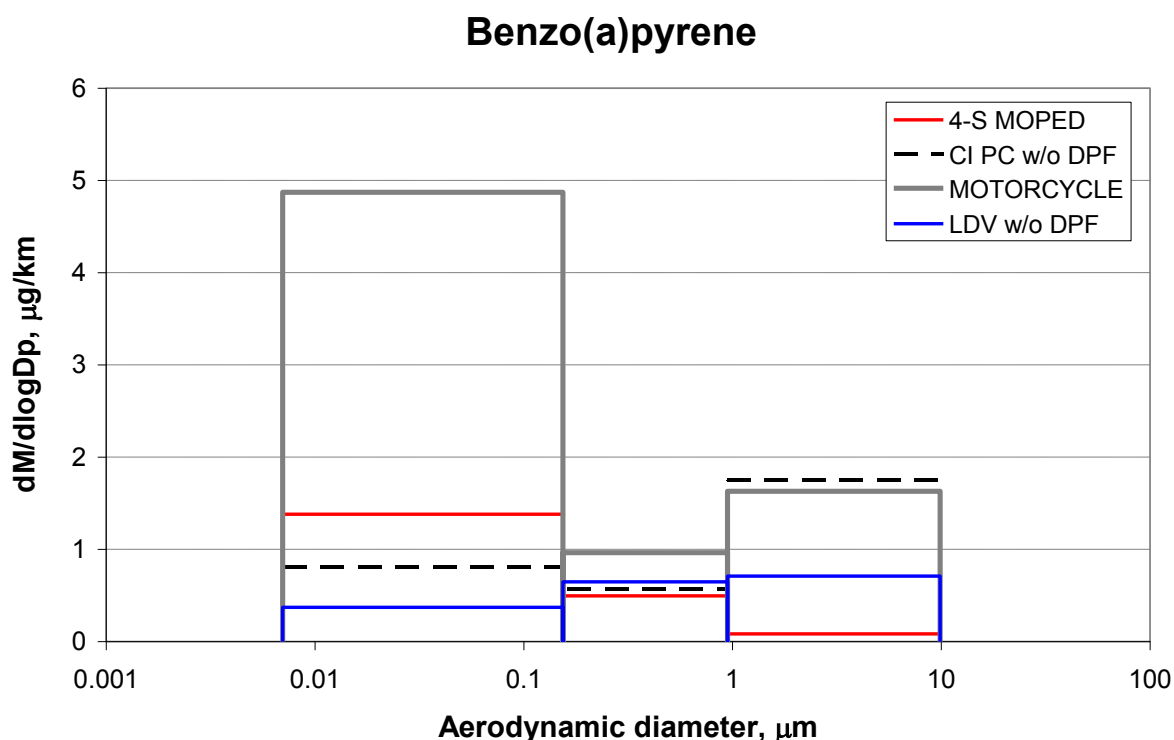


Figure 27. Benzo(a)pyrene size distribution

Benzo[a]pyrene (B[a]p), classified as carcinogenic to humans by IARC, is used as a marker for the carcinogenic risk of PAHs. The method, called Individual PAH method (IPM) estimates a toxic equivalent (TEQ) by summing the environmental levels of each aromatic expressed as “B[a]P equivalents”. These quantities are calculated by multiplying the concentration of single PAH for the carcinogenic potency relative to benzo(a)pyrene, the so called Toxic Equivalency factor – TEF. Figure 28 reports the results of this analysis. In particular, percentage of carcinogenic PAHs and the Toxic equivalent estimated for the tested vehicles is displayed for the three dimensional groups and for the whole dimensional range. Percentage of carcinogenic in total PAHs is very high ranging between 30 and 50 %. The carcinogenic percentage in the different dimensional groups does not follow an unique trend for all the tested vehicles. Despite of this evidence, Toxic Equivalent assumes the highest value in the first dimensional range.

The analysis confirms that the motorcycle emissions of PAHs are not only the highest but also the more dangerous in terms of toxic potency (4 $\mu\text{g/km}$ as total result).

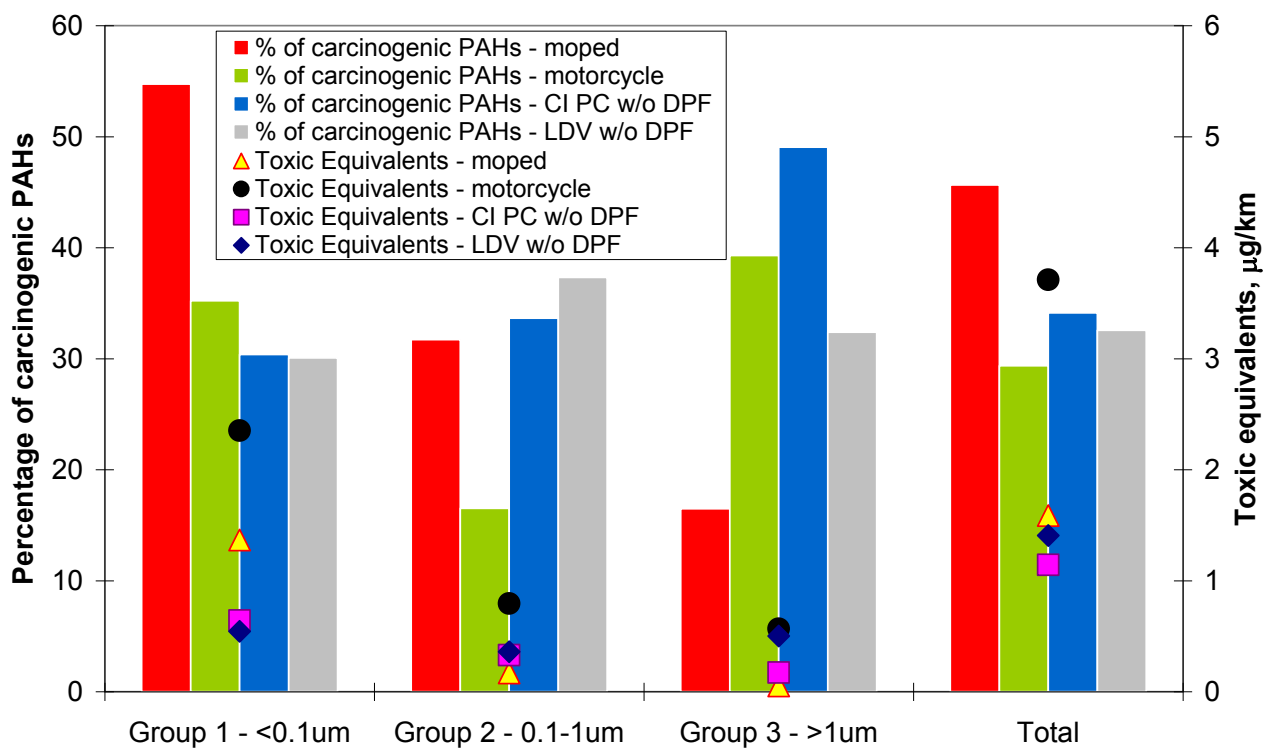


Figure 28. Carcinogenic percentage and toxic equivalents

4.2 Ambient air concentrations

In this section will be presented the results of the ambient air measurements of particulate, PAHs and BTEXs realized in several urban sites of Napoli, during two different experimental campaigns. These ambient air values will be compared with the emissions from the traffic in the next section.

The sampling sites were detailed in Table 4; they include two urban tunnels (T1 and T2), three urban traffic sites (UT1, UT2 and UT3), a sub-urban traffic site (S-UT) and a sub-urban background site (S-UB). The two monitoring campaigns are characterized by different sampling times: during the first one (spatial campaign) air monitoring was realized in all the sampling sites between 12.00 and 13.00, whereas the second one was continuously carried out for almost 14 consecutive days in the same sampling site UT2.

In order to evaluate the spatial distribution of pollutant air concentrations, the data relative to the spatial experimental campaign will be considered together with results of temporal campaign, by extrapolating only data referred to the same hourly range in a day (12.00-13.00). Data acquired during the temporal campaign, instead, allow to have a lot of data referred to the same sampling site. In this way, an hourly and daily analysis of pollutant concentration variations was possible.

Results of each pollutant will be separately discussed.

4.2.1 Particulate

The comparison of ambient air PN concentrations measured in the several sampling sites, expressed as particles/cm³, is reported in the Figure 29. The values correspond to the mean of at least two measurements in the same sampling site. The bars coincide with the evaluated standard deviation.

It is evident that three emission levels are delineated. The first and the highest corresponds to values measured in the tunnel environments ($5-8 \times 10^5$ particles/cm³). Difference of PN concentration in the two tunnels is due to the different traffic flow: tunnel T2 is characterized by a much higher traffic than that measured in tunnel T1. The second level corresponds to the urban traffic sampling sites; in these cases, PN concentration becomes almost 10^5 particles/cm³. The lowest concentrations are detected in sub-urban sites (almost 10^4 particles/cm³).

Assuming the particles as spheres, the particle mass was evaluated. This evaluation needs of the particle density value, which was assumed to be 1 g/cm^3 .

This assumption represents a strong hypothesis on the density value of the particulate; previous studies have, in fact, demonstrated that the particulate density is a function of the particle diameter: higher the diameter, lower the density (Schmid et al., 2007).

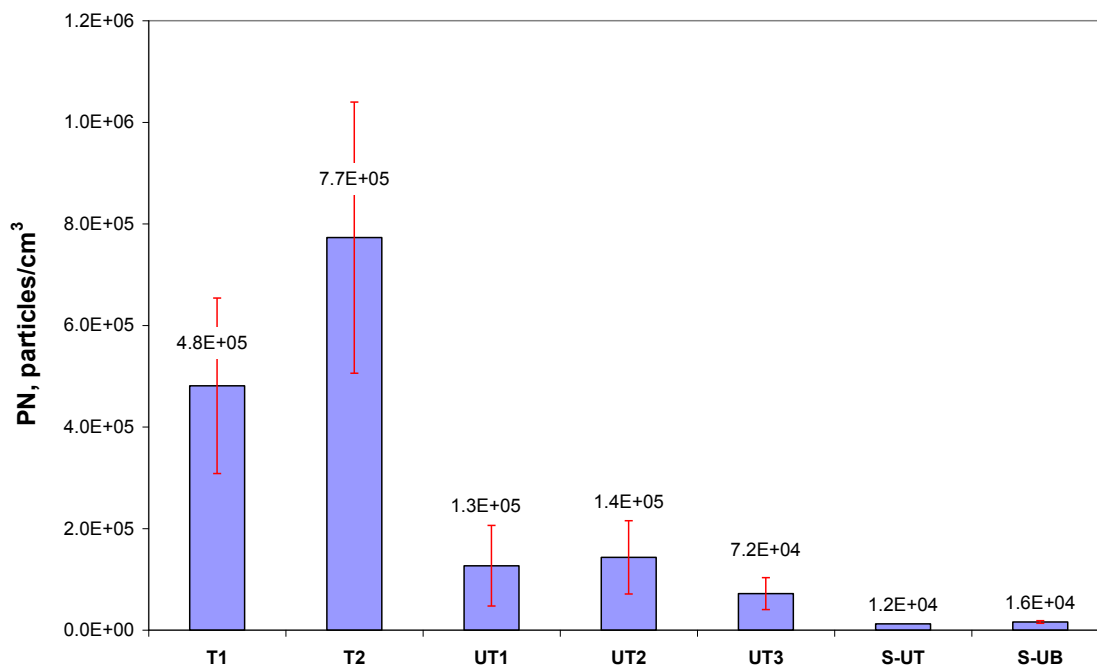


Figure 29. PN air concentrations in sampling sites

Moreover, the inertial impactor is designed to measure the particle number and not the mass; for this reason the mass calculation starting from the particle numbers could be affected by a great error, mostly for the larger particles that more account for the total volume and mass.

In order to restrict the error, only mass of particles with the diameter lower than $1 \mu\text{m}$ (PM1) was estimated.

PM1, reported in Figure 30, follows the same trend of PN. The tunnels are the most polluted sites (150 and $410 \mu\text{g/m}^3$ for T1 and T2, respectively), whereas the lowest value was measured in the background sub-urban site S-UB (almost $6 \mu\text{g/m}^3$).

Figure 31 highlights the difference between PN and PM measured in the Tunnel (T), Urban Traffic (UT) and Sub-Urban (S-U) sites. It graphs the average of measurements referred to the three site

types. It appears evident the decreasing of air particulate when moving from tunnel to su-urban sites.

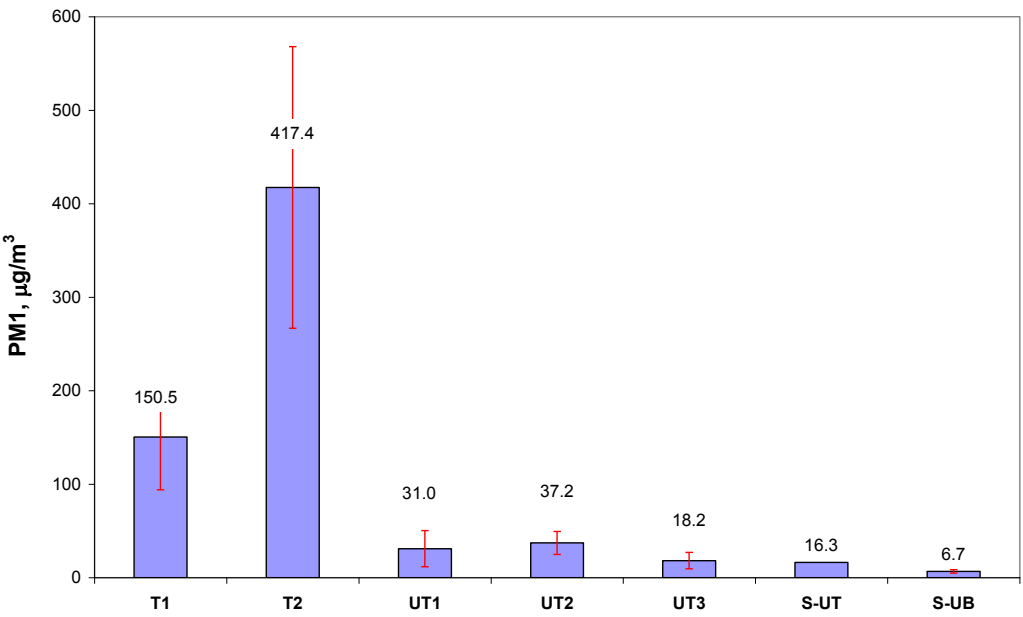


Figure 30 – PM1 air concentration in sampling sites

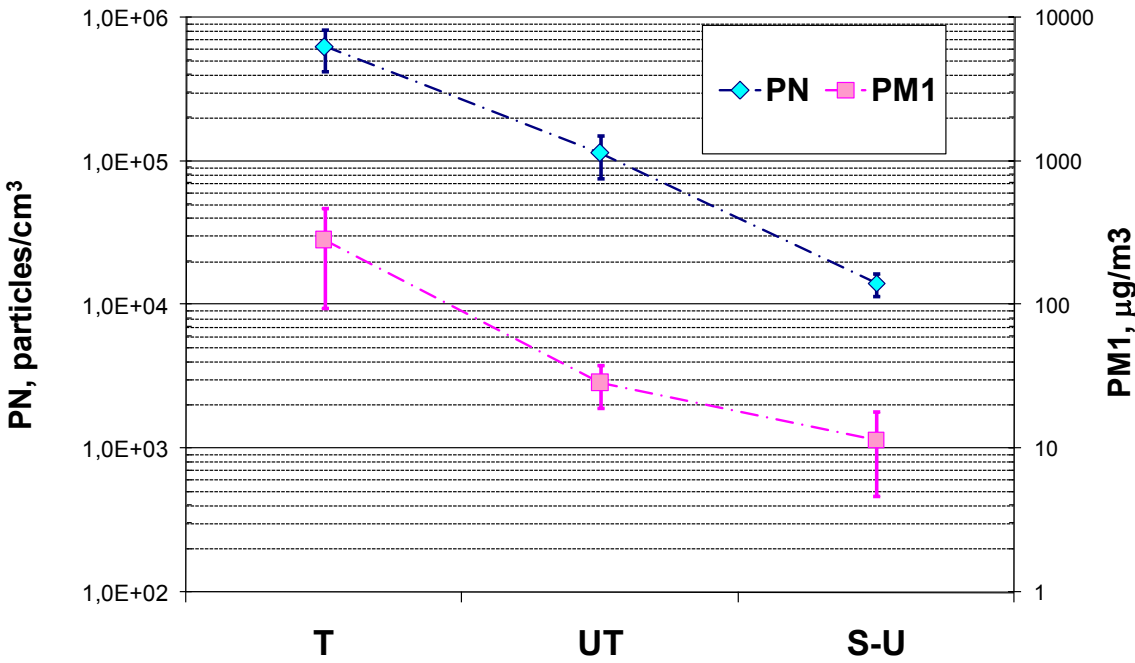


Figure 31 – Average PM and PN concentrations in tunnel (T), Urban traffic (UT) and sub-urban (S-U) sites

The PM1 data evaluated by ELPI were validated comparing them with PM10 and PM2.5 measured by the air quality monitoring stations close to the sampling sites. This comparison was possible for UT1, UT3, S-UT and S-UB sampling sites which are located near the monitoring stations NA06, NA07, NA09 and NA01, respectively. It has to be noted that the PM2.5 is measured only by NA06 and NA07 which are the referent air quality stations for UT1 and UT3 sampling sites.

Results show a very good correlation between ELPI data and PM2.5 measured by monitoring stations UT1 and UT3 (Figure 32).

PM10 is, instead, always higher than PM1 evaluated by ELPI measurements. The ratio varies depending on sampling site. The biggest difference occurs in S-UB sampling site, where the PM10 is almost 5 times higher than PM1 by ELPI.

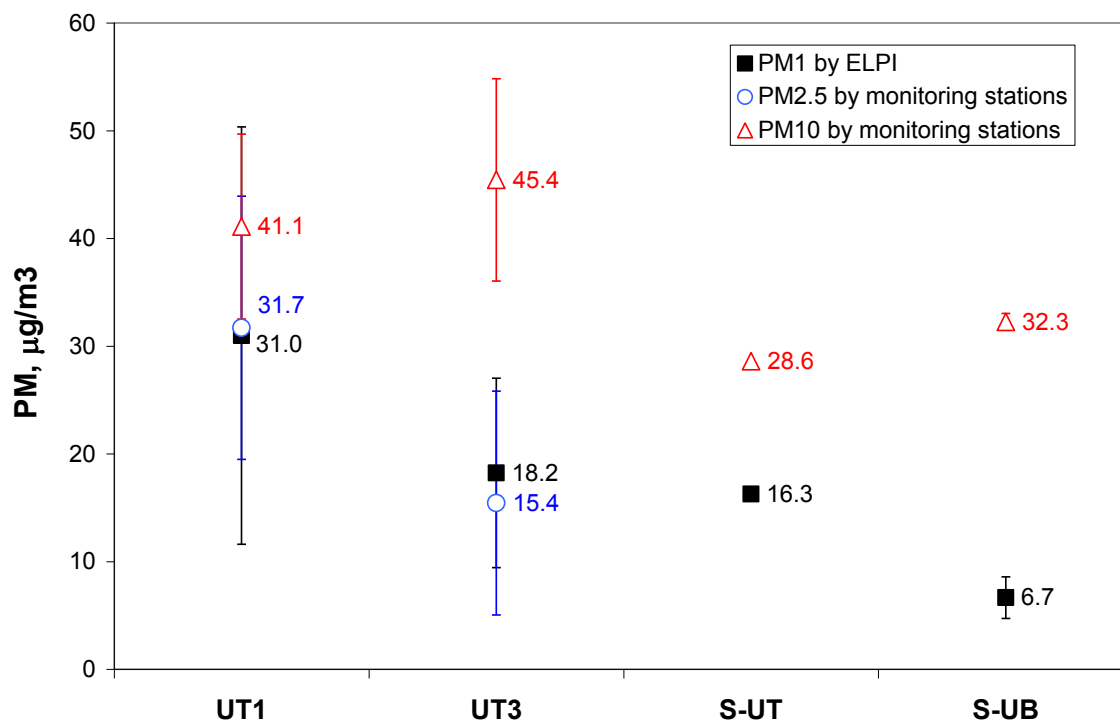


Figure 32 – PM comparison between ELPI measurements and monitoring stations data

The air particulate measured in the three sampling sites (T, UT, S-U) also differ for particle size distribution. Figure 33 summarizes the dimensional distribution of particle number for road tunnel, urban traffic and sub-urban sites. Although all the distributions are modal, the size distribution measured in the tunnel is slightly different in the sense that it peaks at almost 50 nm; those measured in urban and sub-urban sites, instead, have a decreasing trend with the particle diameter,

the peak occurring on the first dimensional stage. The UT and S-U particle size distribution is similar to that measured in Helsinki by Pakkanen et al., 2006.

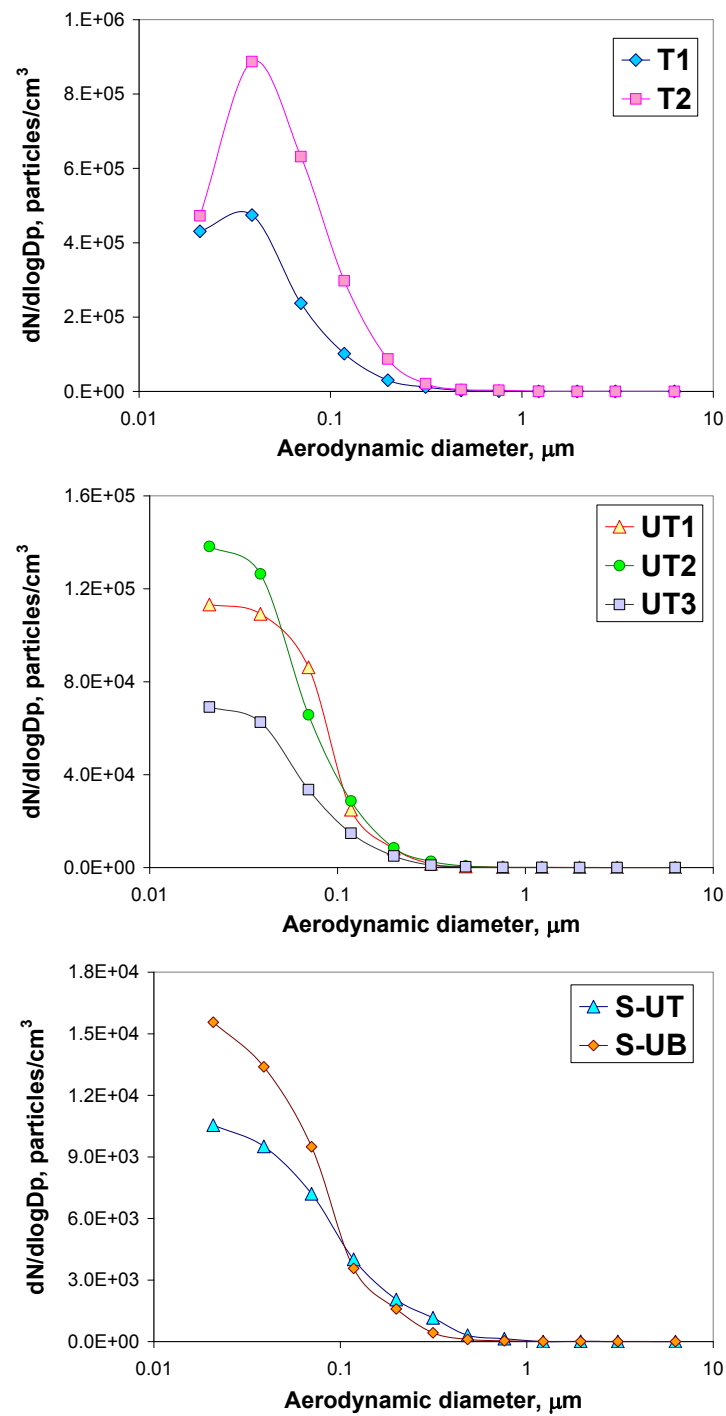


Figure 33. Particle size distribution in ambient air

The analysis of ambient particle distributions measured in all the sampling sites states that almost the 95% of total particle number is represented by particles with the diameter lower than 100 nm; the 100% of the particles has dimensions lower than 1 μm .

Starting from the number concentration data and assuming particles as spheres, surface area and volume distributions were estimated and plotted in Figure 34 and Figure 35. The graphs are log-log plots because of the very different values of the several monitoring sites. Although the different values of total surface observed at the measured particle dimensions, the surface area size distribution has a single mode centered on about 200 nm. This is typical of urban environments (Seinfeld and Pandis, 1998, Lonati and Giugliano, 2006). The volume distribution shows a mode around 200-300 nm, a minimum around 1 μm and for higher diameters an increasing trend, which should suggest the presence of a second mode around 6-10 μm . The normalised distribution of the surface area and volume are reported in Figure 36. The percentage are calculated by dividing the single surface or volume value for the PM₁₀ surface and volume. The surface of PM_{0.1} accounts for about 35% of the total area, PM₁ for about 85%.

The same percentages evaluated for the volume distribution are obviously lower than those relative to the surface: PM_{0.1} accounts for roughly 5% and PM₁ for 40%.

Experimental data of ambient air particulate confirm that the majority of particle number has dimensions lower than 0.1 μm , particle surface in the accumulation mode (0.1-1 μm) and volume and mass divided between the accumulation and coarse (diameters higher than 1 μm) modes (Harrison et al., 2000, Morawska et al., 2008)).

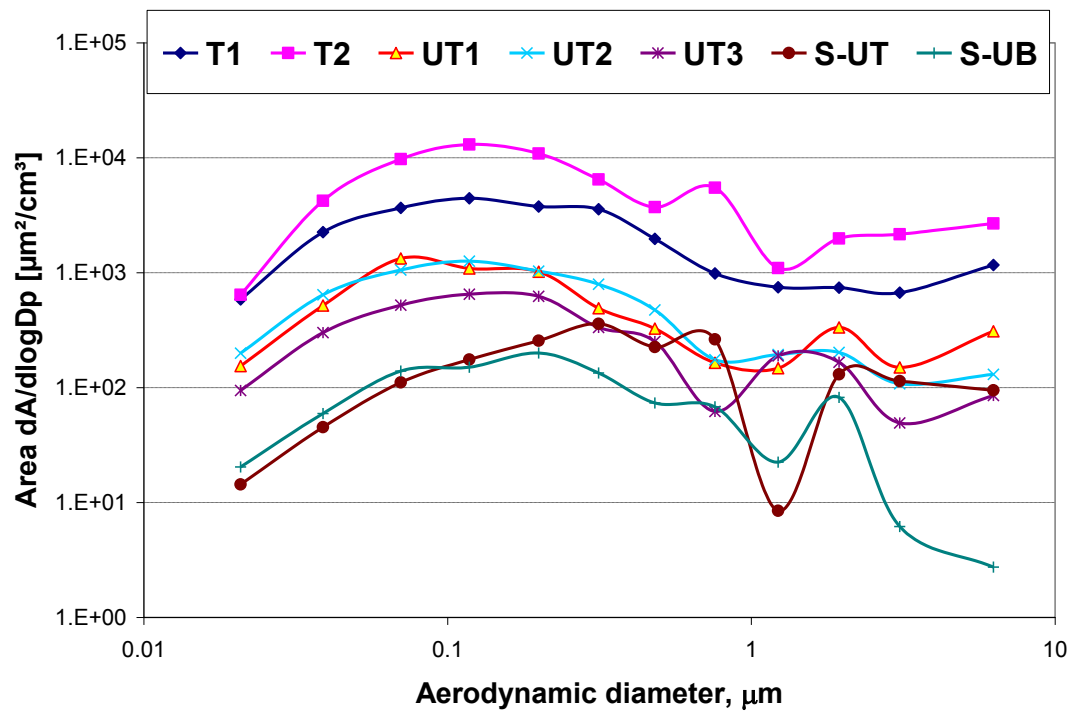


Figure 34. Surface area size distribution in ambient air

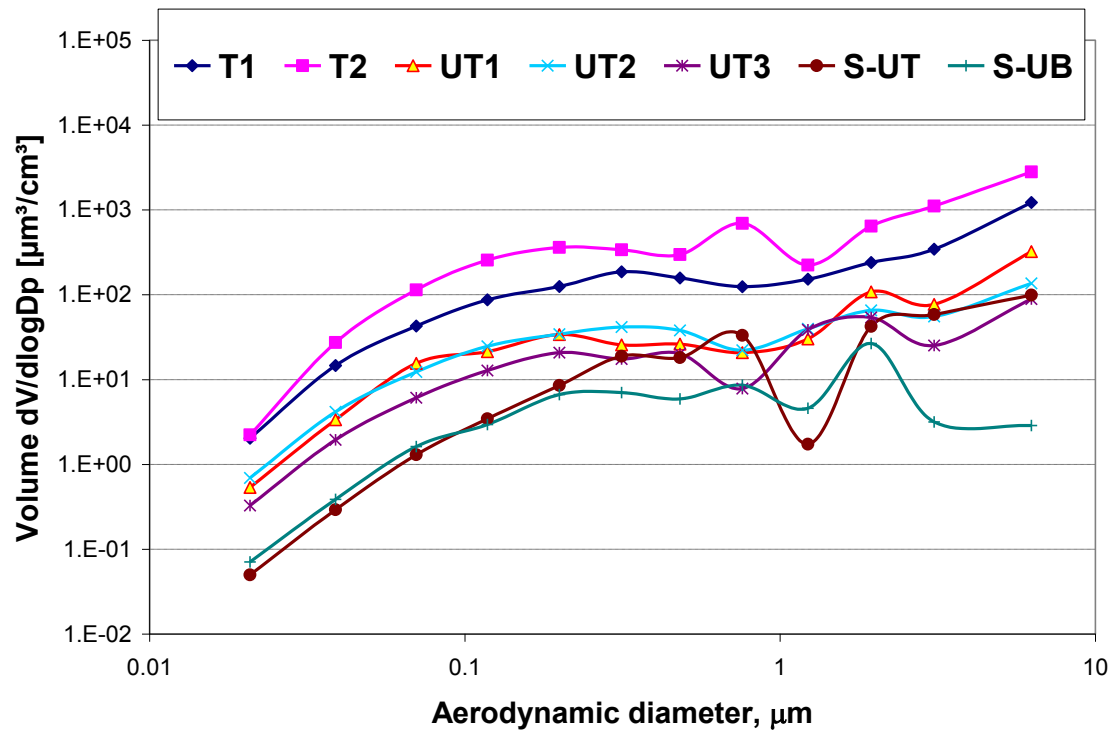


Figure 35. Volume size distribution in ambient air

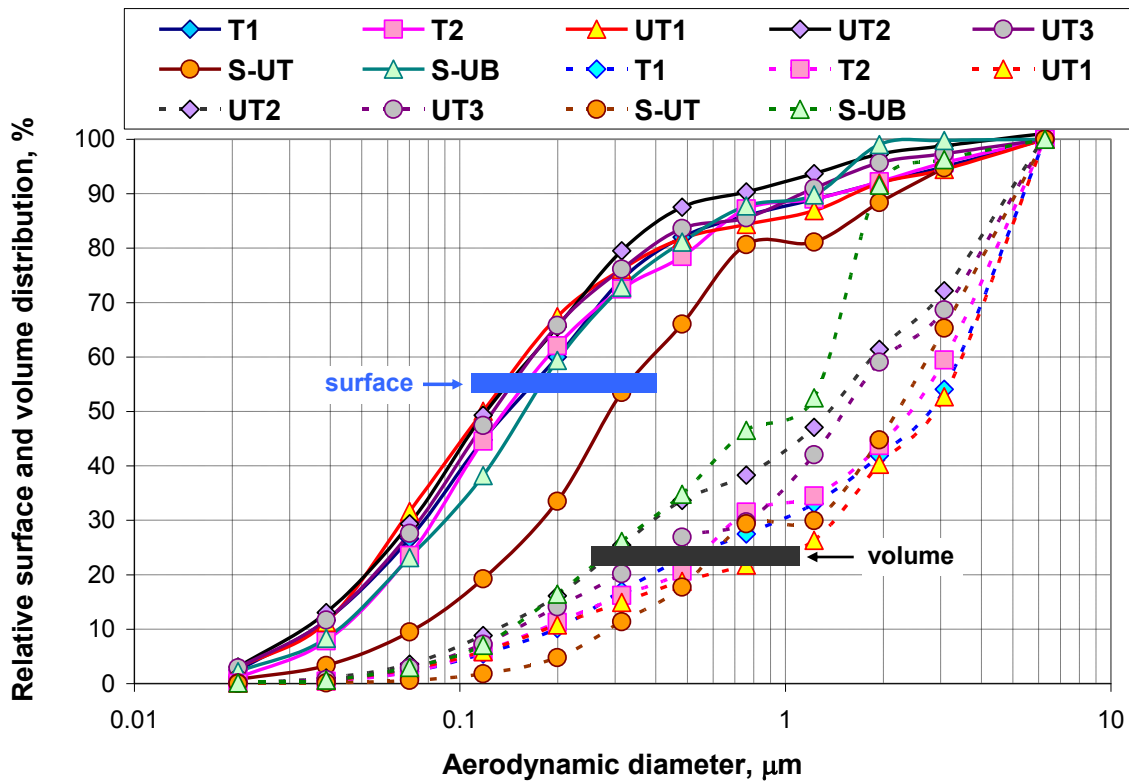


Figure 36. Relative surface and volume distribution

When analyzing measurements carried out over the temporal air monitoring campaign, it is possible to assess an hourly and daily particulate variation. The hourly variation of PN and PM1 monitored in UT2 sampling site is reported in Figure 37. The data from 8.00 to 20.00 correspond to the average, hour by hour, of particle concentration measurements carried out during a typical weekday.

As already discussed in the section 4.2.1.1 the traffic volume in these hours is always very high; the total vehicle flow, in fact, ranges between 1600-2000 vehicles /h.

The PN concentration during the day ranges between 7×10^4 and 1.6×10^5 particles/cm³. Observing the hourly trend, it appears that the PN concentration is almost 10^5 particles/cm³ with the exception of the hours from 10.00 to 11.00 and from 15.00 to 16.00 (where the particle number decreases), and after 18.00 (where the particle number increases).

The Figures also reports the PM1 hourly trend, calculated by ELPI particle number. PM1 concentration ranges between 20-47 μg/m³. The hourly PM1 trend is less variable respect to particle number from which it derives. This behavior is explained by a different particle size distribution. Figure 38 and Figure 39 well highlight the change of particle size distribution occurring during the day.

In Figure 38, the average size distribution recorded in 5 time intervals is reported. The relative contribution of ultra-fine particles measured on the first ELPI dimensional stage changes when moving from the morning to the evening. The average distribution observed from 8.00 to 10.00 is fully decreasing, with the first point of distribution representing the highest PN value. This distribution starts to change from 10.00 to 12.00 where the second point of the particle number distribution becomes comparable to the first one. During the last observation of the day (from 18.00 to 20.00) the peak is shifted and the second dimensional point becomes the highest one.

The variation of particle size distribution during the day is better underlined in Figure 39 where the percentage particle volume distribution is reported hour by hour for the three dimensional classes corresponding to the nucleation mode (diameter lower than $0.1\ \mu\text{m}$), accumulation mode (between $0.1\text{-}1\ \mu\text{m}$) and coarse mode (higher than $1\ \mu\text{m}$). When moving from 8.00 to 20.00, a great increasing (almost twice) of accumulation mode and nucleation percentage is detected at the expense of percentage of coarse mode.

The variation in volume distribution justifies the quite stable trend of the PM₁ respect on PN during the afternoon and evening time. The PM₁ mass, in fact, is mainly influenced by number of particles of accumulation mode rather than nucleation; it changes by varying this relative composition of particle size distribution.

The daily variation of particulate was analyzed by collecting the total PM on the sampling filters. In most cases during the two weeks of the temporal experimental campaign, the sampling time was 2 hours during the day and 12 hours during the night. Due to some unforeseen events, this time schedule, obviously, was subjected to some exceptions.

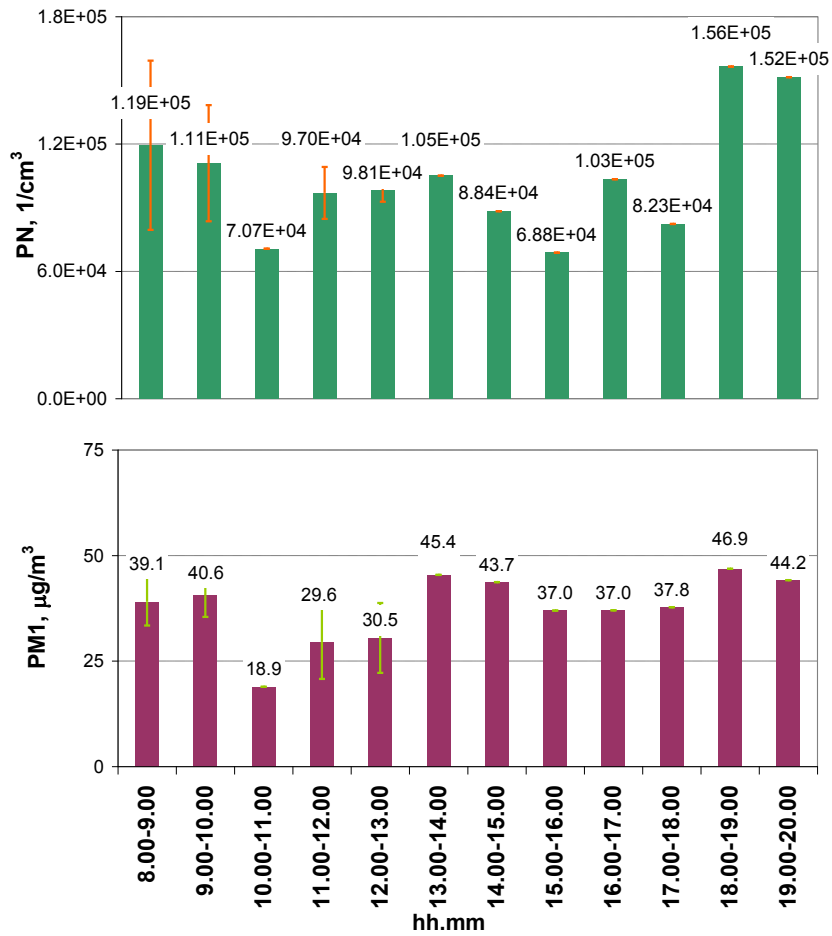


Figure 37. Hourly variation of PN and PM1 measured in UT2 site

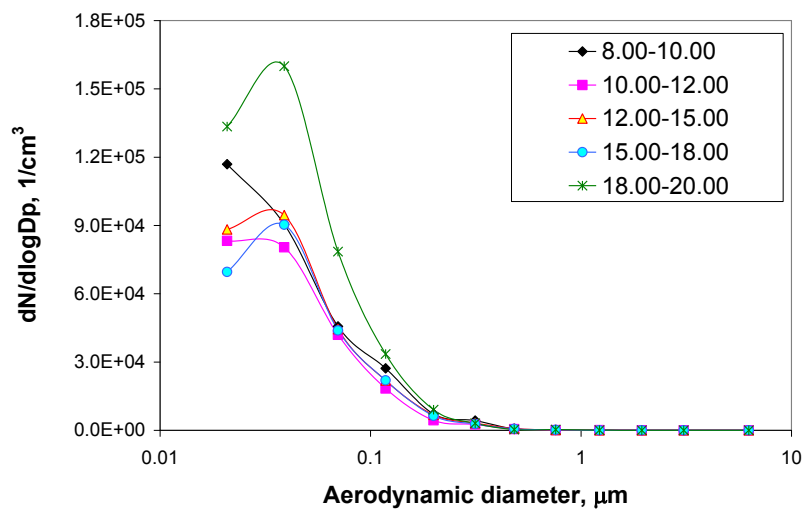


Figure 38. Particle number size distribution in UT2 at different hours of the day

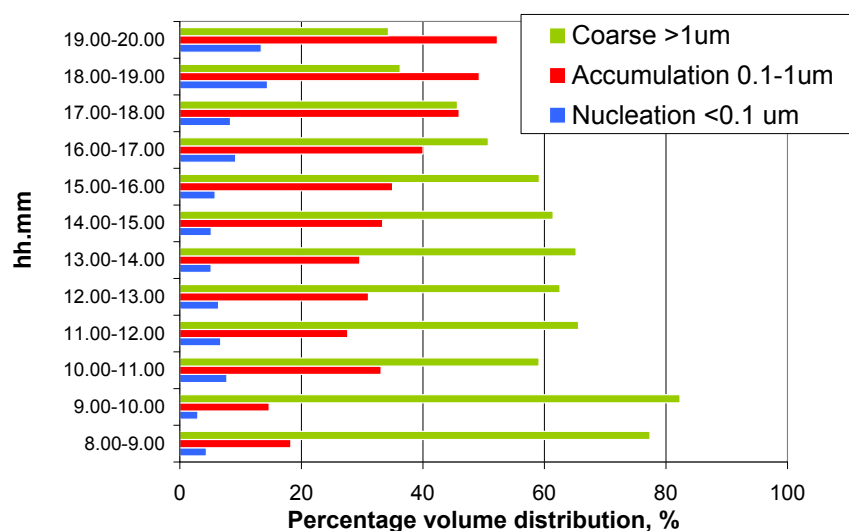


Figure 39. Percentage particle volume distribution in UT2 at different hours of the day

The exact sampling times with the relative PM results are reported in Table 9. First of all, a comparison between the measured PM and the PM10 measured by air quality monitoring station NA06, positioned close to the sampling site UT2, was made. The comparison is showed in Figure 40. The PM measured corresponds to the weight average of the several measurements carried out during a day. The comparison shows a very good agreement with PM10 of air quality monitoring station for some days; for other days, the data are quite different. This happens for example during the week-end days (15/05/10 and 16/05/10); in this last case, the discrepancy is due to weather which during these days was rainy. The rain presence has probably influenced the sampling procedure of PM. In most cases, during the night of the weekdays, PM ambient air concentrations become lower than those measured during the day (Figure 41). With the exception of some days (12/05/2010 and 19/05/2010) during which PM measured during the night and the day are comparable, the particulate concentration measured during the day (from 8.00 to 20.00) is 20-60% higher than particulate measured during the night (from 20.00 to 8.00). These differences in ambient particulate concentrations agree with the traffic volume reduction occurring during the night in this sampling site. The average number of vehicles per hour passing in UT2 during the night is at least 50% lower than the day flow.

| Week Day | Date, dd/mm/yy | sampling from hh.mm to hh.mm | PM, $\mu\text{g}/\text{m}^3$ | Week Day | Date, dd/mm/yy | sampling from hh.mm to hh.mm | PM, $\mu\text{g}/\text{m}^3$ |
|-----------|----------------|------------------------------|------------------------------|-----------|----------------|------------------------------|------------------------------|
| Monday | 10/05/10 | 20-8 | 52.3 | Monday | 17/05/10 | 08-10 | 75.4 |
| Tuesday | 11/05/10 | 08-18 | 80.6 | | | 10-12 | 68.0 |
| | | 20-8 | 35.4 | | | 12-14 | 40.6 |
| Wednesday | 12/05/10 | 08-10 | 39.3 | | | 14-16 | 53.0 |
| | | 12-14 | 54.2 | | | 16-18 | 38.4 |
| | | 16-18 | 45.3 | | | 18-20 | 39.7 |
| | | 20-8 | 47.2 | | | 20-8 | 26.9 |
| Thursday | 13/05/10 | 08-10 | 62.3 | Tuesday | 18/05/10 | 08-10 | 49.1 |
| | | 10-12 | 64.6 | | | 10-12 | 49.8 |
| | | 12-14 | 44.6 | | | 12-14 | 47.2 |
| | | 16-18 | 28.8 | | | 14-16 | 46.3 |
| | | 18-20 | 81.5 | | | 16-18 | 41.6 |
| | | 20-8 | 23.1 | | | 18-20 | 46.0 |
| Friday | 14/05/10 | 08-10 | 48.6 | Wednesday | 19/05/10 | 20-8 | 21.6 |
| | | 10-12 | 14.8 | | | 08-10 | 34.0 |
| | | 12-20 | 46.6 | | | 10-12 | 38.4 |
| Saturday | 15/05/10 | 20-8 | 34.2 | | | 12-14 | 34.1 |
| | | 08-10 | 92.6 | | | 14-16 | 42.4 |
| | | 10-12 | 25.0 | | | 16-18 | 40.7 |
| | | 12-14 | 32.9 | 18-20 | 41.5 | | |
| | | 14-16 | 35.2 | 20-8 | 38.4 | | |
| | | 16-18 | 34.1 | Thursday | 20/05/10 | 08-10 | 67.8 |
| 18-20 | 23.7 | 10-12 | 73.5 | | | | |
| 20-8 | 18.1 | 14-16 | 56.6 | | | | |
| Sunday | 16/05/10 | 08-10 | 219.2 | | | Friday | 21/05/10 |
| | | 10-12 | 181.0 | 20-8 | 45.2 | | |
| | | 12-14 | 30.8 | 08-10 | 77.0 | | |
| | | 14-16 | 34.8 | | | 10-12 | 60.8 |
| | | 16-18 | 26.6 | | | | |
| | | 18-20 | 30.8 | | | | |
| | | 20-8 | 16.1 | | | | |

Table 9. PM concentration in UT2 site

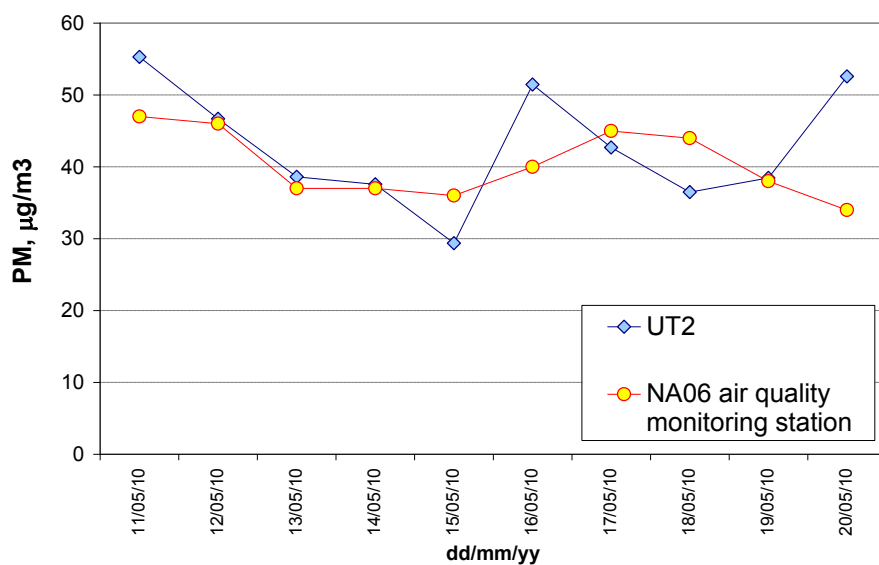


Figure 40. Comparison of measured daily PM in UT2 with PM10 of air quality monitoring station

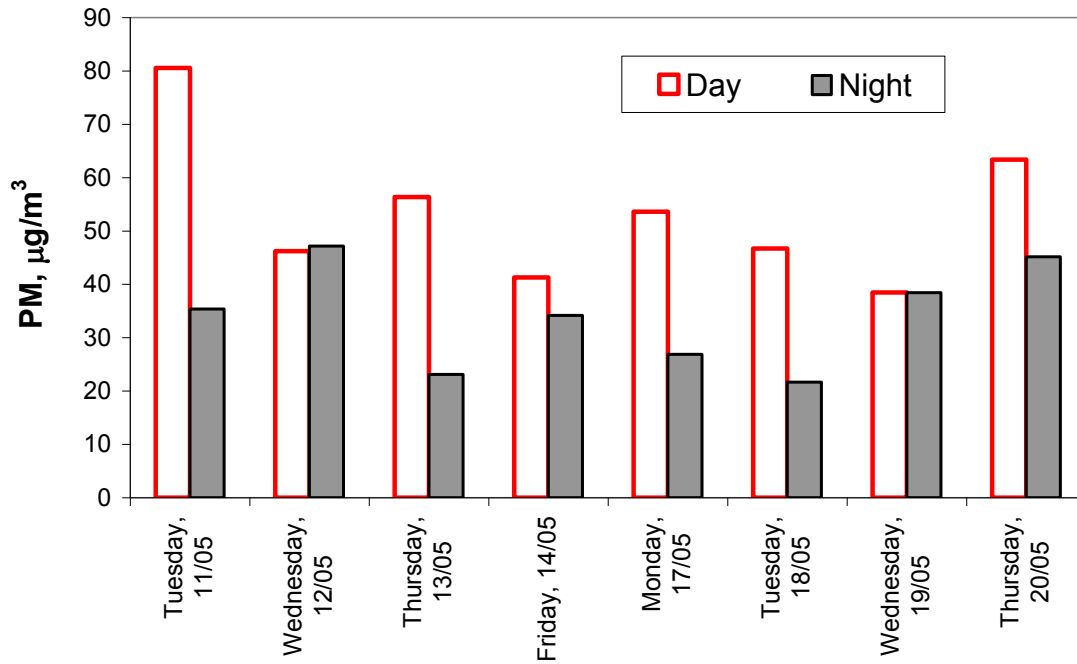


Figure 41. Night/Day PM ambient air concentrations

Measurements in UT2 were repeated in cold and warm seasons. This aspect has allowed the study of the seasonal variation of particle concentration in air. In order to make a reliable comparison, only the data from 11.00 to 13.00 were considered.

The comparison of seasonal data points out that in the cold season the total number of particles is about two times greater than in the warm season (Lonati et al., 2006, Pakkanen et al., 2006). The ratio between the PM1 estimated by ELPI measurements is almost 1,7 (Table 10).

| | PN, 1/cm ³ | dev st | PM1, mg/m ³ | dev st |
|----------------------------------|--------------------------|---------|------------------------|--------|
| Cold Season (Dec 2009) | 2.3E+05 | 2.9E+04 | 51.5 | 0.3 |
| Warm Season (May 2010) | 9.8E+04 | 7.7E+03 | 30.0 | 7.0 |

Table 10 – Seasonal PN and PM1 comparison in the urban site UT2

The seasonal difference in particle number is detailed in particle size distribution reported in Figure 42. The percentage of particle number reduction is reported stage by stage. For particles with a diameter lower than 200 nm the reduction is almost 60%, it goes down at almost 20% for larger particles. By considering the variability of data, the difference between the particle number measured during the warm and cold season is mainly due to the nucleation mode.

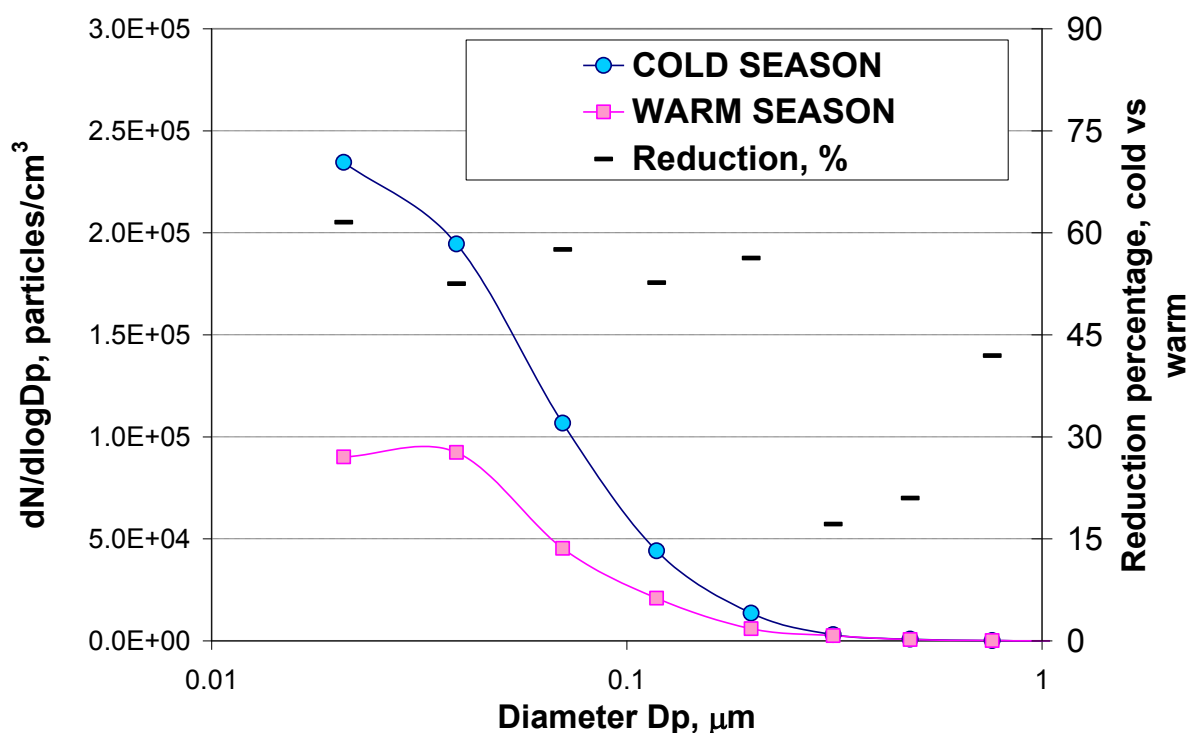


Figure 42 – Seasonal variation of observed particle size distribution in the urban site UT2

4.2.2 Polycyclic Aromatic hydrocarbons

The content of PAHs in particulate phase was evaluated also for ambient air sampling.

The Figure 43 summarizes the mean PAHs concentrations measured in the several sampling sites. The trend for PAHs is not so clear as for the other pollutants. Emission levels of the several sampling sites are, in fact, quite comparable. They range between 250 ng/m³ measured in the road tunnels and almost 120 ng/m³ measured in the sub-urban background sampling site. The levels measured in the other sites vary between 120-200 ng/m³.

The same Figure reports the PAHs results grouped according the three sampling sites types (T, UT and S-U). This graphs better explains the PAHs differences; in particular, it is evident that although the average values are different, only the difference between PAHs measured in tunnel and sub-urban sites is statistically significant. The percentage of the carcinogenic compounds is relatively high (30-45%) with benzo(a)pyrene covering almost 5% of the total. The Table also reports the toxic potential expressed as benzo(a)pyrene equivalents. It appears that the B(a)P equivalents is

mainly composed by the B(a)P compound which represents between 60-80% of the total toxic potential.

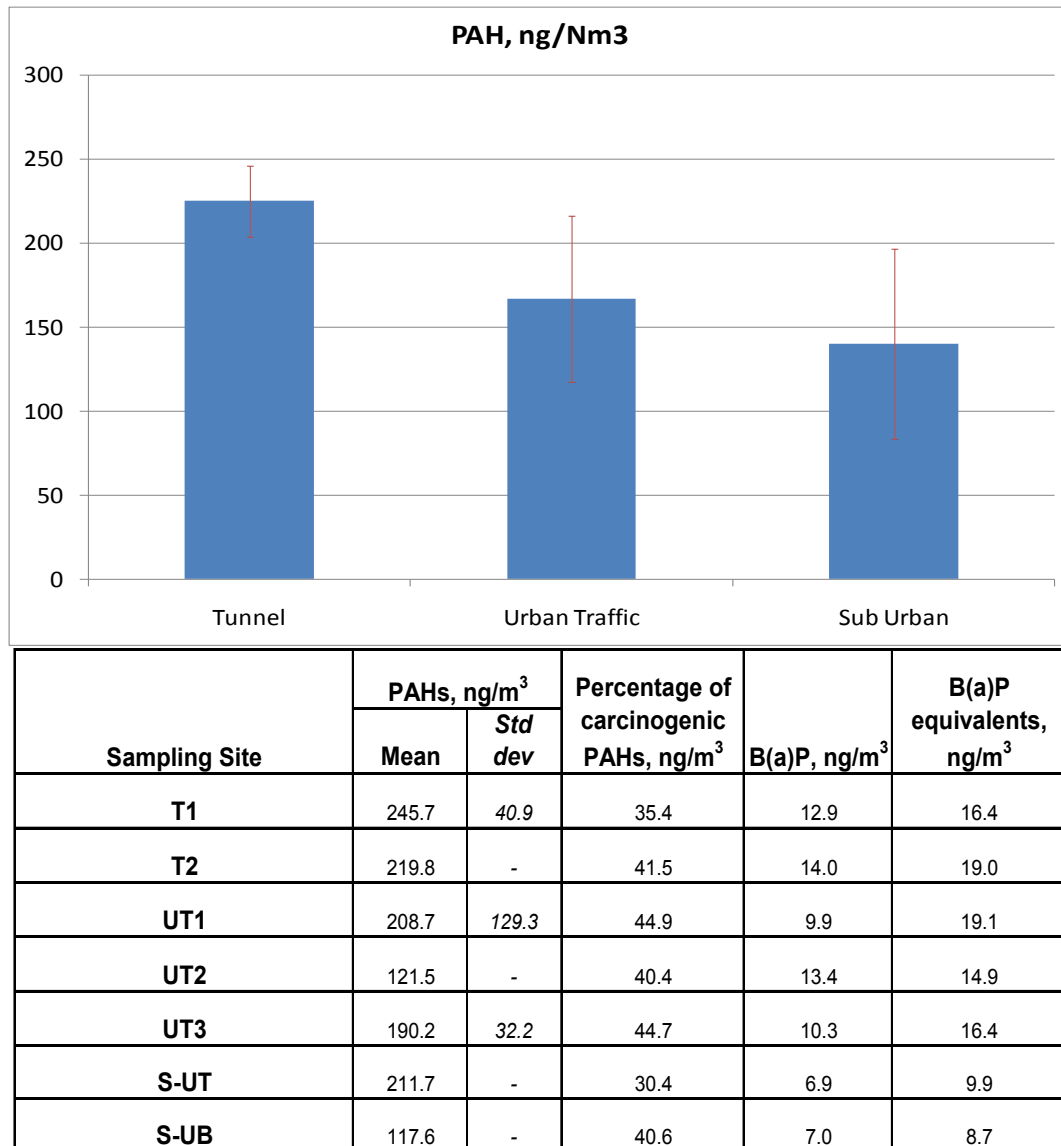


Figure 43. PAHs particle bounded in ambient air

Looking at the size distribution of PAHs in the three dimensional groups corresponding to the nucleation, accumulation and coarse modes, the highest content of PAHs was almost always bounded to the particles with the diameter higher than 0,1 μm . This behavior is visible in Figure 44, where PAHs size distributions are reported for the road tunnels (T), the urban traffic (UT) sites and sub-urban (S-U) sites. With the exception of S-UB site having a decreasing PAHs size distribution, for other sites the highest PAHs content was measured in accumulation or coarse modes.

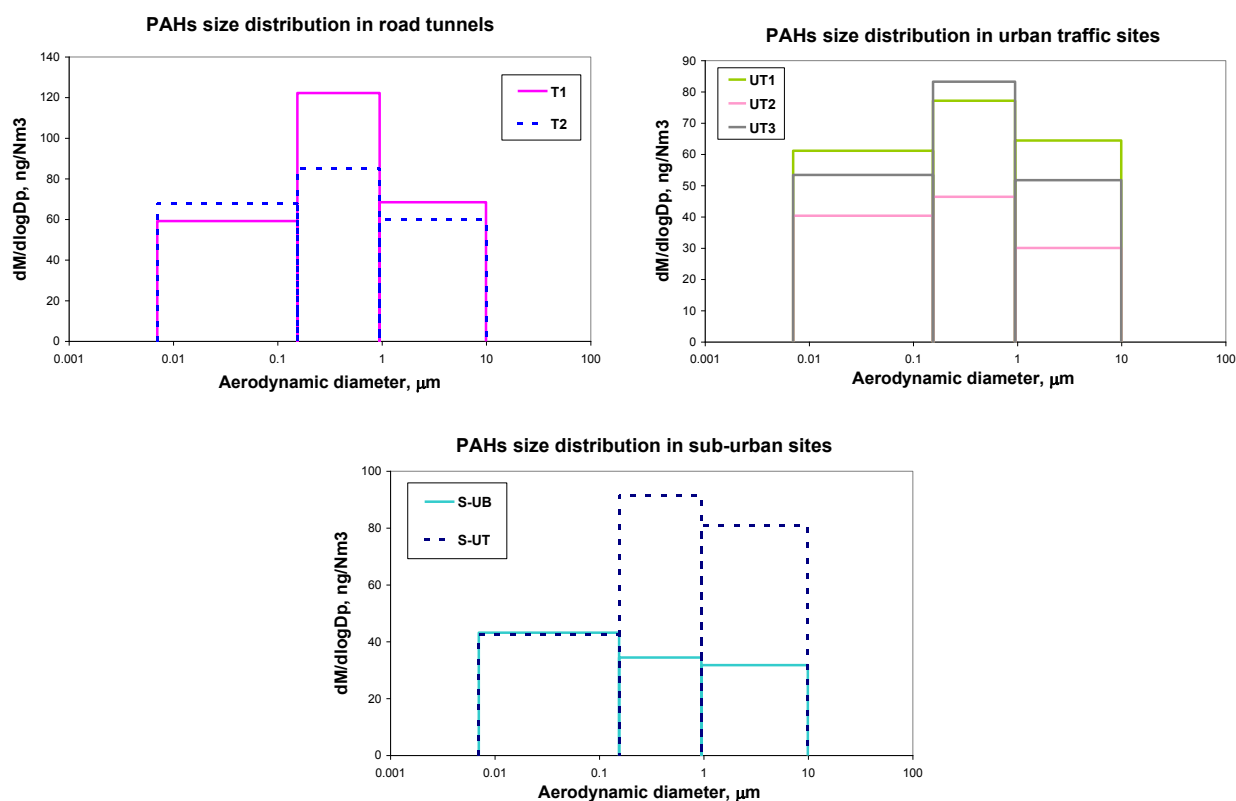


Figure 44. PAHs size distribution in ambient air

The chemical characterization of ambient air particulate presented above is referred to the spatial experimental campaign. During the temporal one, some ELPI filters of the measurements in UT2 site were also extracted to characterize the PAHs content in particulate phase during different days and different hours of the day. In particular, samplings from 8.00 to 10.00 and from 14.00 to 16.00 of three weekdays (18, 19 and 20 may) were considered to analyse the daily and hourly PAHs variation. The comparison between the total PAHs concentration measured in different days has not showed significant differences. The average daily PAHs concentration ranges between 150 – 200 ng/m³ with a percentage of carcinogenic compounds covering between 30-40% of the total.

The hourly distribution of PAHs on the three different dimensional groups is the same already seen in Figure 44. The Figure 45 displays the PAHs size distribution of the two sampling hours (from 8.00 to 10.00 and from 14.00 to 16.00). It is evident that the first dimensional stage (particles with the diameter lower than 0,1 μm) have the lowest PAH content. The PAHs concentration in the coarse mode is the highest during 14.00-16.00 sampling and is comparable with accumulation one for 8.00-10.00 sampling.

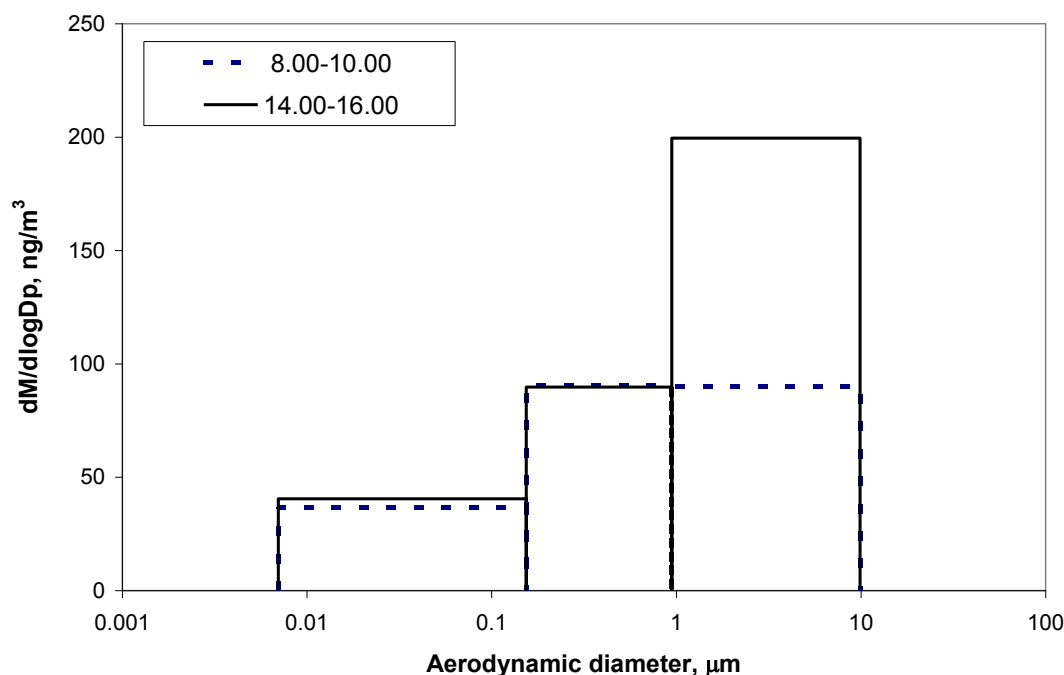


Figure 45. PAHs size distribution in ambient air

4.2.3 BTEX

Besides the measurements carried out in UT2 sampling site during the temporal campaign, BTEX (Benzene, Toluene, Ethylbenzene, o-/m-/p-xylene) concentrations were evaluated also in T1 site (Galleria delle Quattro Giornate) in the period from February 2008 to February 2009. The samplings were realized in part in the morning (at almost 9.00) and in part in the evening (at almost 15.00).

Samples were collected at the middle of the tunnel which is long almost 600 m, positioning two parallel sorbent tubes at almost 2 m of height from road surface. During each measurement, ambient temperature was monitored in order to normalize at standard conditions the sampling flow.

Results obtained by this experimental campaign are reported in Figure 46. Figure reports the single measurements, the mean and the standard deviation of all samplings for each compound, expressed as $\mu\text{g}/\text{Nm}^3$. More abundant components are toluene and the sum of m- and p- xylene, which analytical methods doesn't allow to separate. The mean value of benzene is higher than actual standard value. Road tunnel data agree with Na, 2006, whose results, referred to Seul, indicate the

same BTEX distribution (B almost $48 \mu\text{g}/\text{Nm}^3$, T $120 \mu\text{g}/\text{Nm}^3$, EB $19 \mu\text{g}/\text{Nm}^3$ m-+p-X $96 \mu\text{g}/\text{Nm}^3$ and o-X $25 \mu\text{g}/\text{Nm}^3$).

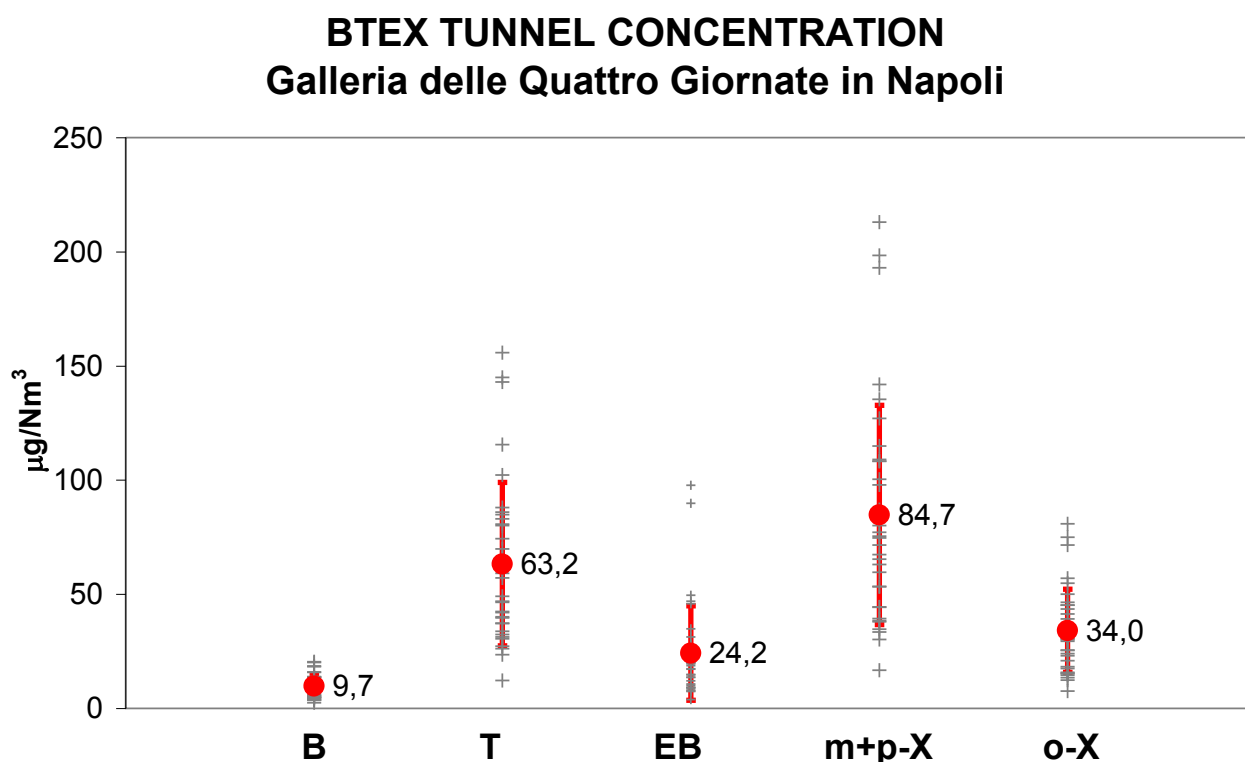


Figure 46. BTEXs concentrations measured in road tunnel T1 (Feb-08 Feb-09)

The BTEXs results referred to UT2 sampling site are reported in Figure 47. Data points correspond to 8 measurements carried out for a day, for 8 weekdays during the spring experimental campaign. It is very interesting to note that the relative distribution of the single compounds exactly reflects that measured in road tunnel T1.

Also in the ambient air of the open urban traffic sampling site UT2, the most abundant compounds are toluene and the sum of m- and p-xylene isomers. The less abundant is benzene with a mean concentration equal to almost $3.5 \text{ mg}/\text{m}^3$ which is lower than the actual air quality standard limit. The measured values in UT2 are very similar to those of previous experimental campaigns carried out in Napoli (Murena, 2007, Iovino et al., 2008).

In general, it is possible to state that the average BTEXs concentrations in UT2 are the half of those measured in the road tunnel T1.

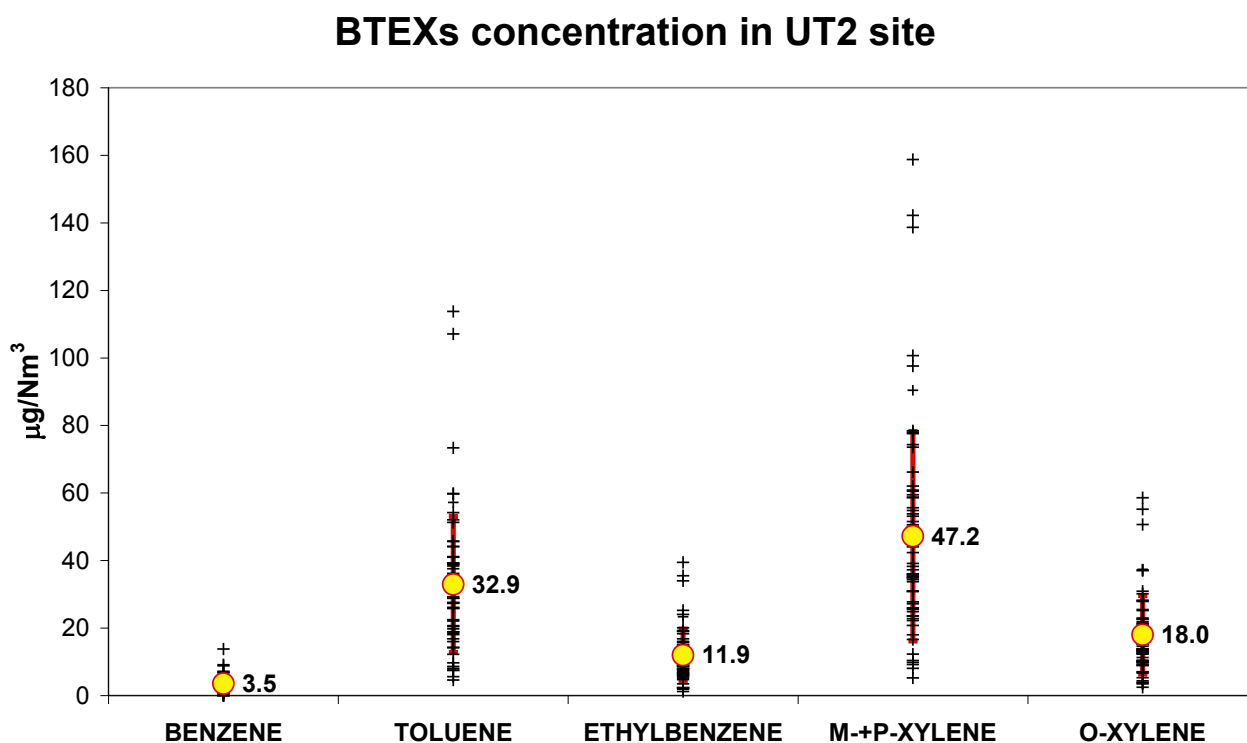


Figure 47. BTEXs concentrations in UT2 sampling site

Measurements of BTEXs in UT2 were executed from 8.00 to 18.00 during a day. As already done for the other pollutants, the availability of a lot of data collected in different hours of the day and referred to the same sampling site allows to make an analysis of the hourly variation of the single compound. The hourly trends of the single BTEX concentrations are reported in Figure 48. The trend of the average values is similar hour by hour for all the compounds. The highest concentrations of each BTEXs, in fact, are measured around the 8.00 and the 19.00, whereas the minimum concentrations are positioned between 12.00 and 17.00. Moreover, another aspect joining all the compounds is the high variability of the data referred to the last sampling of the day (around 19.00).

BTEX measurements carried out within this research activity were compared with literature, by comparing BTEX ratios. Because of the varying reaction rates of VOCs with hydroxyl radical, these ratios provide information about the difference of origin source in the environment. The abundance of highly reactive VOC species usually decreases in daylight time due to photochemical reactions. On the other hand, the abundance of relatively less reactive species gradually increases during daylight time due to accumulation (Simpson, 1995).

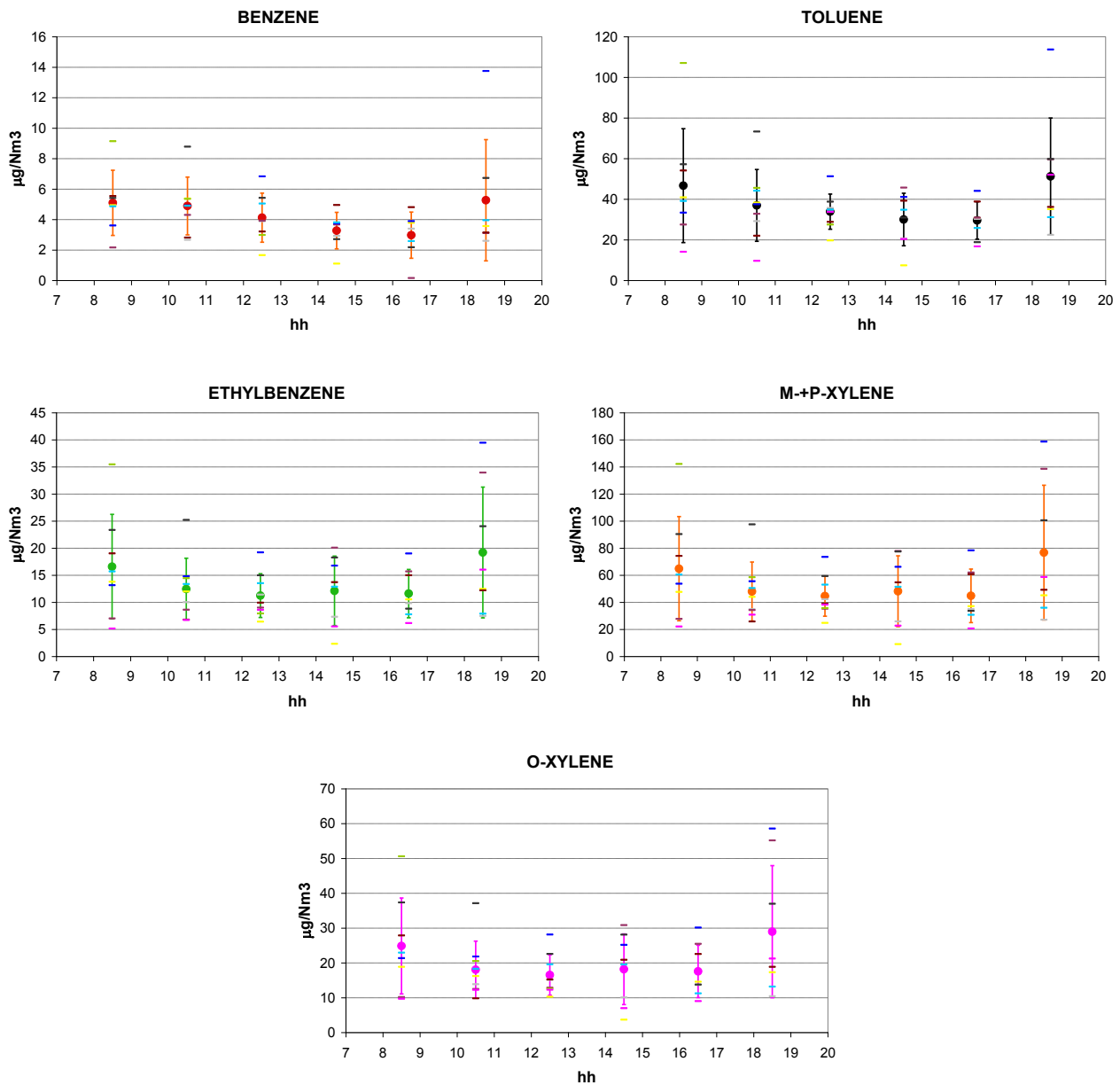


Figure 48. BTEXs hourly variations in UT2 sampling site

Table 11 summarizes BTEX ratio taken by several research papers. Among all, a valid indicator for the pollution source is the mixing ratio m-/p-xylene/ethylbenzene. With the exception of Caselli et al., 2010 and Iovino et al., 2008, data found in the literature show that this ratio, evaluated in traffic sites, is ranging from 2,9 to 4,0. In this study the m-/p-xylene/ethylbenzene ratio showed a mean value of 3,8, confirming the vehicular traffic source.

| BTEX ratio | T/B | EB/B | m+p-X/B | o-X/B | EB/T | m+p-X/T | o-X/T | m+p-X/EB | o-X/EB | o-X/m+p-X |
|--|------------|-------------|----------------|--------------|-------------|----------------|--------------|-----------------|---------------|------------------|
| Tunnel T1 in Napoli - Costagliola, 2010 | 6,5 | 2,5 | 8,7 | 3,5 | 0,4 | 1,3 | 0,5 | 3,5 | 1,4 | 0,4 |
| Urban Traffic UT2 in Napoli - Costagliola, 2010 | 12,1 | 4,8 | 19,1 | 7,5 | 0,4 | 1,4 | 0,6 | 4,0 | 1,5 | 0,4 |
| Urban Traffic open sites in Napoli - Iovino et al, 2008 | 0,9 | 0,9 | 0,8 | 0,9 | 0,9 | 0,8 | 0,9 | 0,9 | 1,0 | 0,8 |
| Tunnel exit in Napoli - Murena, 2007 | 12,1 | 4,1 | 14,8 | 5,1 | 0,3 | 1,2 | 0,4 | 3,8 | 1,3 | 0,3 |
| Urban Traffic open sites in Munich - Rappengluck et al, 1998 | 1,7 | - | 0,7 | - | - | 0,4 | - | 2,9 | - | - |
| Urban Traffic open sites in Cairo - Matysik et al, 2010 | 2,6 | 0,4 | 1,4 | 0,5 | 0,2 | 0,5 | 0,2 | 3,5 | 1,1 | 0,3 |
| Urban Traffic open sites in Algeri - Kerbachi et al, 2006 | 1,6 | 0,1 | 0,3 | - | 0,1 | 0,2 | - | 3,6 | - | - |
| Urban Traffic open sites in Rio de Janeiro - Martins et al, 2007 | 4,4 | 3,3 | 9,5 | 2,7 | 0,8 | 2,2 | 0,6 | 2,9 | 0,8 | 0,3 |
| Urban Traffic open sites in Dehli - Hoque et al, 2008 | 2,0 | 0,2 | 0,6 | 0,3 | - | - | - | - | - | - |
| Urban Traffic open sites in Bari - Caselli et al., 2010 | 1,0 | 0,9 | 0,9 | | 1,0 | 1,0 | | 1,0 | | - |

Table 11. Literature review of BTEX ratios

When looking at the other TEX ratios, there is a good correspondence with the literature for EB/T, X/T, X/EB and xylenes ratios. Ratios to benzene, instead, are higher than literature ones. The reason is probably an under-estimation of benzene concentration which causes the increased ratios of T/B, EB/B, X/B.

4.2.4 Conclusions about air monitoring

Pollutant concentrations measured in ambient air of Napoli have allowed to classify the sampling sites in three groups: tunnel (T), Urban Traffic (UT) and Sub-Urban (S-U). Mean values of PN and PAHs decrease when moving from T to S-U, even though the differences between the sites differs for the two pollutants. In particular, PN measured in tunnel is almost one order of magnitude higher than that measured in UT and two orders of magnitude higher than that measured in S-U. The decreasing percentage is almost 98% between T and UT and almost 90% between UT and S-U. The same behaviour is followed by PM, whose concentration values agree with PM_{2,5} provided by air quality monitoring stations. PAHs differences measured in the several sampling site are smaller than PN ones (almost 30 between T and UT and 12% between UT and S-U). BTEXs measurement, performed in tunnel T1 and urban traffic site UT2, indicate that T values are almost twice higher than UT ones. In both sites, BTEX ratios confirm that they are mainly emitted in the atmosphere by the exhaust vehicle. Results about ambient air particle size distribution highlights that the majority of particle number has dimensions lower than 0.1 μm , particle surface is included in the accumulation mode (0.1-1 μm) and volume and mass divided between the accumulation and coarse (diameters higher than 1 μm) modes. The chemical characterisation of particulate shows that major PAHs content is bounded to particles with diameter higher than 0,1 μm .

4.3 Correlation between ambient air concentrations and exhaust emission rate

This section is dedicated to the correlation between the measured pollutant ambient air concentrations, discussed in the previous Section, and the emission rate from real traffic flow in several sampling sites of Napoli. The comparison concern the pollutants quantified in ambient air during the monitoring campaigns: BTEXs (Benzene, Toluene, Ethylbenzene and Xylenes isomers), the particle number concentration, the particle size distribution and the PAHs bounded to the particulate phase. First of all, the Section 4.3.1 will detail the methodology used for estimating the emission rate of exhaust pollutants in ambient air. In this Section the input data needed for this calculation will be discussed: the traffic characterization in terms of volume and composition and the pollutant exhaust emission factors. The emission rates of all involved pollutants will be eventually reported. The ambient air data will be compared with emissions in the Section 4.3.2 which discusses both the quantitative and qualitative correlation between the pollution air and traffic source.

4.3.1 Exhaust pollutant emission rate

In order to compare ambient pollution in urban areas with traffic source, pollutant emission rate has to be estimated.

This calculation needs, first of all, of the knowledge of traffic flow in each urban sampling site; the traffic should be characterized in terms of vehicle category (passenger cars, two-wheelers, light-duty and buses), fueling type (diesel, gasoline, natural gas), type-approval stage (from pre-Euro to Euro 5). This grouping allows to define for each vehicle group the right emission factor (grams of pollutants emitted for driven kilometer) and, consequently to calculate the emission rate coming from that vehicle category. The whole exhaust emission rate produced in each traffic situation is the sum of several contributions relative to the different vehicle groups.

Indeed, the emission flow rate of the pollutant p (M_p), expressed as g/h, is calculated:

$$M_p = \sum_i n_i f_{e_{pi}} L \quad 4.2.1$$

Where

i is the vehicle category

n_i is the number of vehicle per hour for each vehicle category

fe_{pi} is the emission factor of the pollutant p for each i vehicle category, g/km

L is the length of sampling site (this computation will be applied for the length of 1 km)

In other words, in order to estimate the exhaust emission rate by real urban traffic the following input data are needed:

1. Urban traffic flow grouped in vehicle categories (passenger cars, two wheelers vehicles, light duty vehicles and buses);
2. Composition of circulating fleet in Napoli city in terms of fuel, type approval stage for all vehicle classes;
3. Emission factors in g/km of each pollutant and for each vehicle class.

The experimental campaigns have allowed the monitoring of traffic flow, grouped as reported in 1. But, in-situ traffic measurements did not provide the composition of circulating fleet in terms of fuel type and type approval stage. This classification was obtained by statistics on circulating Italian fleet by Automobile Club d'Italia-ACI, referred to Comune di Napoli (ACI, 2009).

Concerning the emission factors of measured pollutants (BTEX, PN, PAHs), it has to be pointed that the experimental work for characterizing exhaust emissions, carried out within this PhD thesis, was very important to provide emission factors for these unregulated species; literature, in fact, gets poor data about the emission factors of these micro-pollutants and there is a lack of data for new technology vehicles. The pollutant exhaust characterization, discussed above, greatly cover the lack of data, most of all for the composition of tested fleet which include very new technologies.

Each input data for this calculation will be detailed in the following.

4.3.1.1 Monitored traffic in several sampling sites of Napoli

Traffic flow and composition were monitored during each ambient air measurement. The spatial distribution of traffic flow measured in the several sampling sites is represented in Figure 49. During the hours of observations (12.00-13.00) the urban sites, including the tunnel, are characterized by a total traffic volume ranging between 2000-3000 vehicles/h. It has to be pointed that the data of T2 is underestimated because, although the tunnel has two directions, only the traffic along one direction was measured. Indeed, the traffic flow of T2 reported in Figure is almost

the half of the total number of vehicles circulating in this tunnel. The data for S-UT is missing because the sampling site was positioned in a pedestrian zone bordering the traffic zone; for this reason, it was not possible to easily frame the traffic with the video camera. The S-UB is, instead, located in a park away from the traffic, so the vehicular flow is zero.

Due to the availability of data in the same sampling site UT2, it was possible to measure the temporal distribution of total traffic flow during a day. The results are graphed in Figure 50 which reports the total traffic flow from 0.00 to 24.00. Data points correspond to the average, hour by hour, of traffic measurements carried out during ten weekdays. It is evident that the UT2 site is characterized by a high daily traffic volume: from 8.00 to 20.00 the total vehicle flow, in fact, ranges between 1600-2000 vehicles/h. In this temporal interval, the maximum flow was monitored at almost 13.00 whereas the minimum around the 11.00.

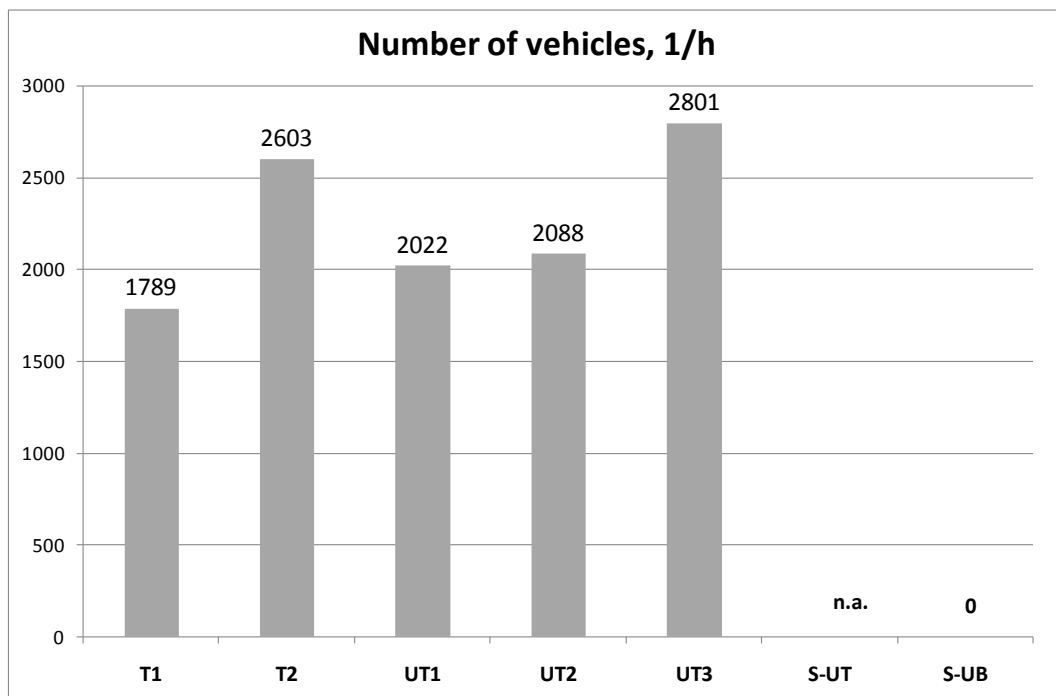


Figure 49. Spatial traffic flow distribution

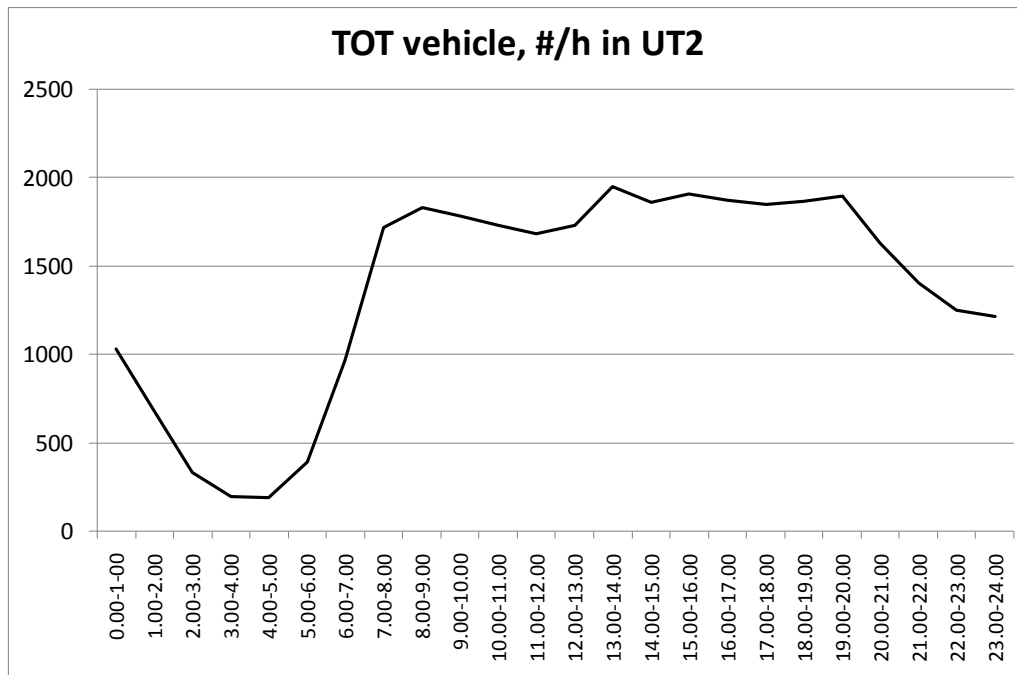


Figure 50. Daily traffic flow distribution in UT2

Starting from 21.00, the traffic volume rapidly decreases, up to reach the minimum value (almost 200 vehicles/h) at 4.00 during the night.

In order to investigate about the correlation between the traffic emissions and air quality, it is very important to characterize the traffic composition, in terms of number of vehicles belonging to a specific vehicle category. During the experimental campaign, the traffic monitoring carried out by using a video camera, has allowed to group the vehicles in the following categories: passenger cars (PC), powered-two wheelers (PTW), light-duty vehicles (LDVs) and buses.

The mean composition of traffic monitored in urban tunnels and open urban sampling sites (UT1, UT2 and UT3) is reported in Figure 51. The Figure shows the percentage contribution of passenger cars, two-wheelers, light-duty vehicles and buses to the total traffic. In most cases, the highest percentage (between 46 and 64%) is covered by the passenger cars. The PC flow is comparable with that of two-wheelers which represent between 30 and 50% of the total traffic. The remaining percentage (lower than 10%) is covered by the sum of buses and light-duty vehicles.

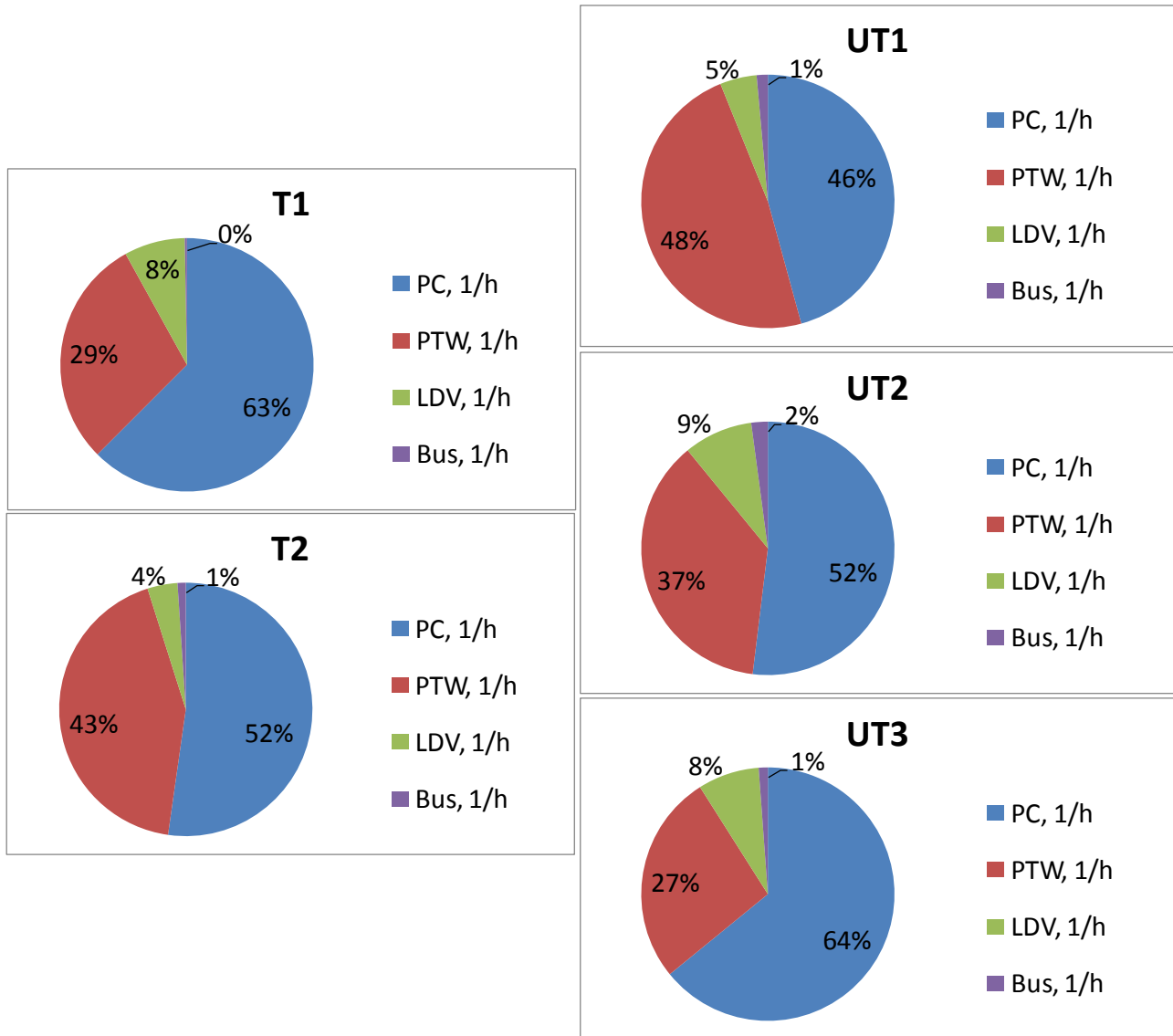


Figure 51. Traffic composition

The analysis of the daily traffic composition in UT2 sampling site states that the percentages relative to each vehicle category do not greatly change from 8.00 to 20.00. It is very similar to that above discussed in Figure 51. The PC cover, in fact, almost 50 % of total flow, the PTW between 40 and 45%, the buses almost 2-4% and LDV almost 3-6% (Figure 52). Outside of this temporal window (i.e. from 20.00 to 8.00) the traffic composition changes; a sensible reduction of PTWs percentage, in fact, was detected. This category represents, in fact, almost 40% of total flow at almost 21.00 and becomes almost 10% at 4.00 during the night. Another percentage variation is monitored for LDV. This category presents the maximum values (7-10%) in the percentage traffic composition between 6.00-13.00 and then decreases at almost 4% during the afternoon and night.

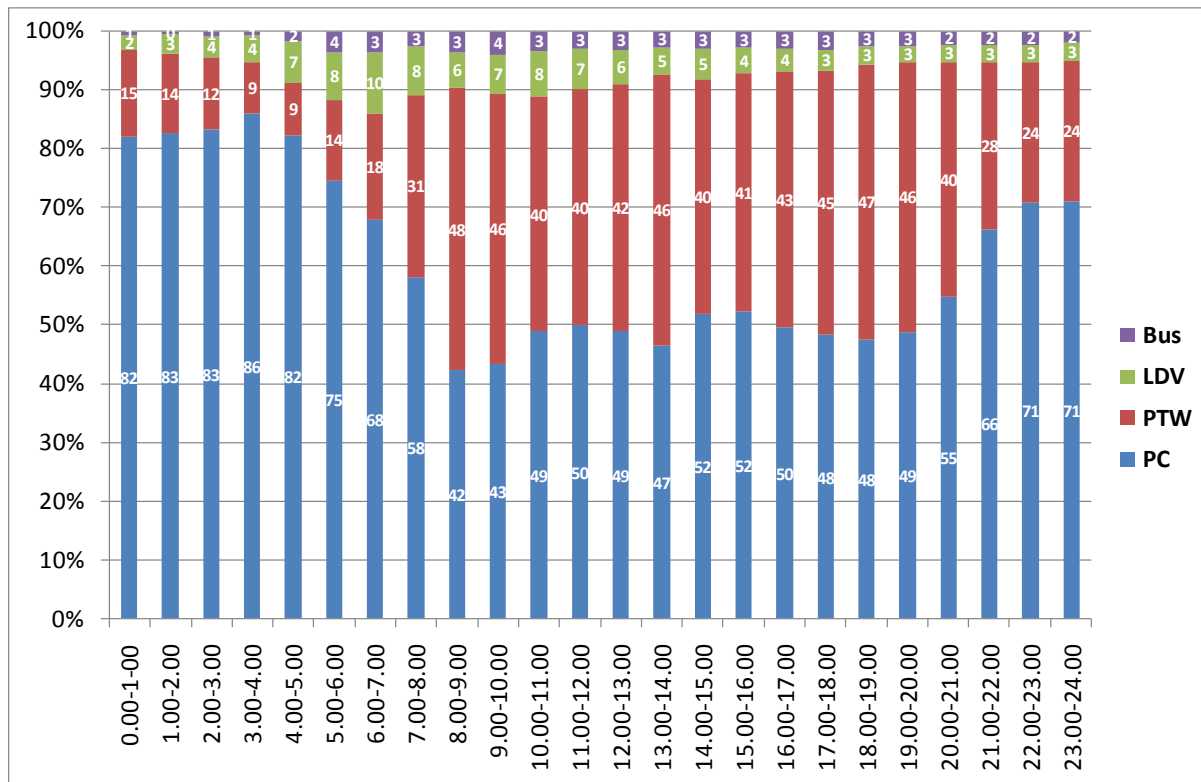


Figure 52. Daily traffic composition in UT2

4.3.1.2 Circulating fleet in Napoli

According to the ACI statistics, the circulating fleet in Napoli is composed by almost 73% of PCs, 22% of PTWs, 5% of LDVs and 0,2 % of buses. This composition differs from that measured in the several sampling sites in Napoli mainly for the percentage of PTW (Figure 53). In fact, the experimental measurements have highlighted a percentage of PTWs higher than the statistical data. This category covers between 23-50% of total vehicle flow. The difference is represented by the number of PC: ACI statistics provide a PC percentage higher than that really measured. The difference between the composition of ACI statistics and the experimental observations are mainly explained by a different average moving speed of PC and PTW. In congested traffic situation, in fact, PTW move more fast than PC, increasing the relative observed vehicle flow. Moreover, although the statistics indicate that PC numbers is higher than PTW one, the use of two-wheelers is preferred to that of four-wheelers in cities such as Napoli characterized by a fine wheatear during the most part of the year.

The statistical data provided by ACI were used to characterize the composition of several vehicle categories in terms of fuel and type approval stage. This grouping is necessary to calculate the emission rate produced by each vehicle group.

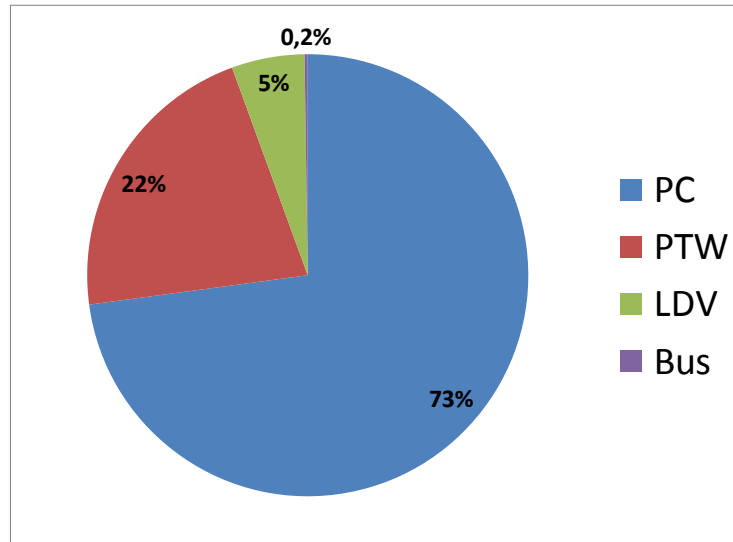


Figure 53. Circulating fleet in Comune di Napoli, ACI 2009

The category of passenger cars (PC) are fueled with gasoline or bi-fueled (gasoline/Liquid Petroleum Gas-LPG or gasoline/Compressed Natural Gas-CNG) for almost 67% (Figure 54). The remaining percentage are diesel vehicles. The age of circulating PC is quite old, and statistical composition states that gasoline fleet is older than diesel one. Almost 70 % of gasoline PC are homologated before 2000 (Euro 3 type approval stage) respect 30% of diesel vehicles. PC which are old less than 5 years (i.e. belonging to Euro 4 and Euro 5 stages) are almost 15% for gasoline group and almost 37% for diesel one.

Concerning the two-wheelers, mopeds (vehicles with engine capacity of 50 cm³) represent almost 36% of the total. The other part is covered by motorcycle category. Among these, almost 70% have an engine capacity lower than 250 cm³. In the last years, in fact, there was a large diffusion of so called “scooter” (small engine capacity two-wheelers) used mainly for urban travels. The age of motorcycle circulating fleet is reported in Figure 55 which represents the percentage of motorcycles grouped on the basis of type-approval stage. New Euro 3 motorcycles (starting from 2005) cover almost 25% of total. This category is composed by a large percentage (50%) of vehicles homologated before 2000 (Euro 2 stage).

LDV category is mainly fuelled with diesel fuel (almost 87%). But, the age of circulating LDV fleet is different from PC one. It is older than that relative to passenger cars. Euro 4 LDV, in fact, are almost 13% of total, which is a percentage very lower than that already discussed for diesel PC.

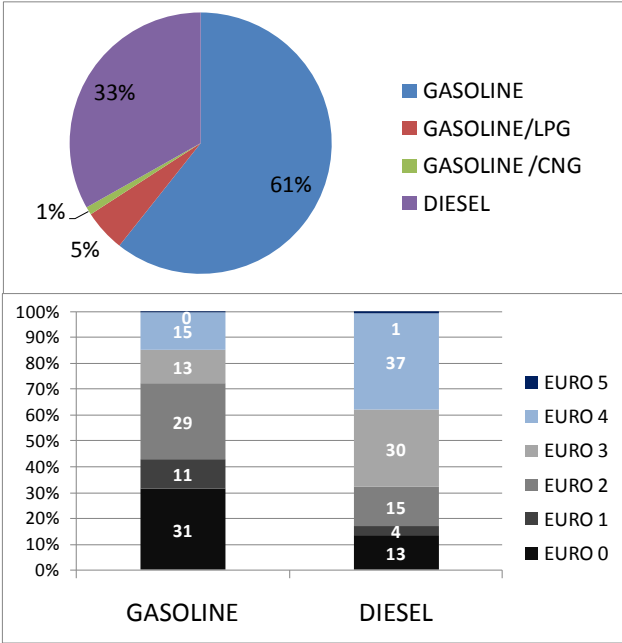


Figure 54. Composition of passenger cars fleet in Napoli (ACI, 2009)

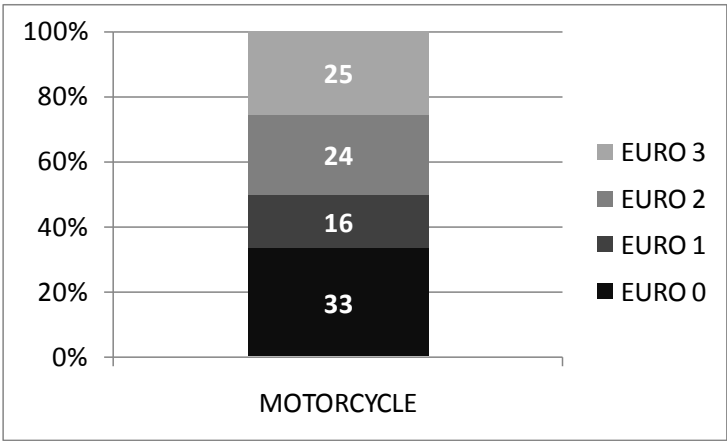


Figure 55. Composition of motorcycle fleet in Napoli (ACI, 2009)

4.2.1.3 Exhaust emission factors

The exhaust measurements carried out inside this experimental work have enriched the emission factors database existing in literature, about particle number and PAHs. As already highlighted it is very difficult to found in research papers these unregulated emission factors. The existing exhaust

data are mostly referred to regulated pollutants and, moreover, few data are available for new technology vehicles. The exhaust results of PAHs and PN measured during this research activity were used as emission factors for estimating emissions produced by several vehicle categories. It has to be pointed that these measurements, although precious, are few compared with the number of vehicle categories. This is particularly true for PAHs data. For this reason, some assumptions about PAHs emission factors were needed for covering the lacking of data. For example, PAHs emission factor of gasoline PC was calculated as the average of available data referred to SI engine motorization. Although this hypothesis should appear not entirely correct, it is the most reasonable solution among the whole opportunities. For diesel PCs, LDVs and PTWs (both motorcycle and moped) the emission factors already showed in Table 8 were used. The buses contribution was not considered in this computation because of the absence of emission factors for all considered pollutants. This omission was possible because the associated error is negligible due to the very low number of buses observed during in-situ measurements.

PN emission factors provided by this experimental work were more numerous than PAHs data, making more complete the characterization of vehicle exhaust; indeed, no assumption were made for this pollutant. PN emission factors were reported in Table 5.

The comparison between the traffic emissions and ambient air concentrations was carried out also for BTEX. Whereas both exhaust and air measurements of PN and PAHs pollutants were performed within the experimental activity, BTEXs characterization was realized only in ambient air. For this reason, the exhaust emissions were fully taken by literature. The lack of exhaust emission factors is also evident for BTEXs. The available literature does not cover the whole vehicle categories (Aakko et al., 2006, Prati et al., 2009, COPERT, 2010).

This aspect has forced to make some assumptions when BTEXs data were lacking. In particular, for light duty vehicles, BTEXs emission factor were put equal to mean values of diesel passenger cars and for two wheelers, xylenes isomers equal to mean values of gasoline passenger cars. Even if both assumptions are suggested by the real fuel type used by light-duties and two wheelers, the last assumption probably introduces an error for the estimation of xylenes emission factors, because two wheelers emissions are generally much higher than those relative to passenger cars.

The BTEX emission factors used for computing emission rate are summarized in Table 12.

All the emission factors of PN, PAHs and BTEXs were weighted according the composition of circulating fleet, in order to calculate the emissions produced by each vehicle category (PC, LDV and PTW). Results are showed in Figure 56, where single compounds are graphed. PN is reported on a separate axis due to the very different values. They constitute the input data for the 4.2.1 formula, leading to the estimation of exhaust emission rate produced by monitored traffic.

| | | Benzene | Toluene | EthylBenzene | m+p-Xylene | o-Xylene |
|-------------|----------|---------|---------|--------------|------------|----------|
| PC gasoline | pre Euro | 45,34 | 208,08 | 47,27 | 65,86 | 44,7 |
| | Euro 1 | 18,14 | 14,34 | 9,43 | 110,2 | 26,55 |
| | Euro 2 | 6,25 | 13,17 | 8,48 | 199,39 | 39,52 |
| | Euro 3 | 1,47 | 2,6 | 2,18 | 62,22 | 6,43 |
| | Euro 4 | 0,3 | 0,2 | 0,19 | 0,54 | 0,23 |
| PC diesel | pre Euro | 8,7 | 34,5 | 8,51 | 36,2 | 9,9 |
| | Euro 1 | 5,2 | 14,2 | 1,23 | 10 | 2,4 |
| | Euro 2 | 1,5 | 3,6 | 6,29 | 68,2 | 17,6 |
| | Euro 3 | 3,3 | 8,9 | 6,94 | 120,2 | 41,6 |
| PTW | | 20 | 120 | 62 | 87,64 | 23,48 |
| LDV | | 4,7 | 15,3 | 5,7 | 58,6 | 17,9 |

Table 12. BTEXs emission factors of PC, LDV and PTW

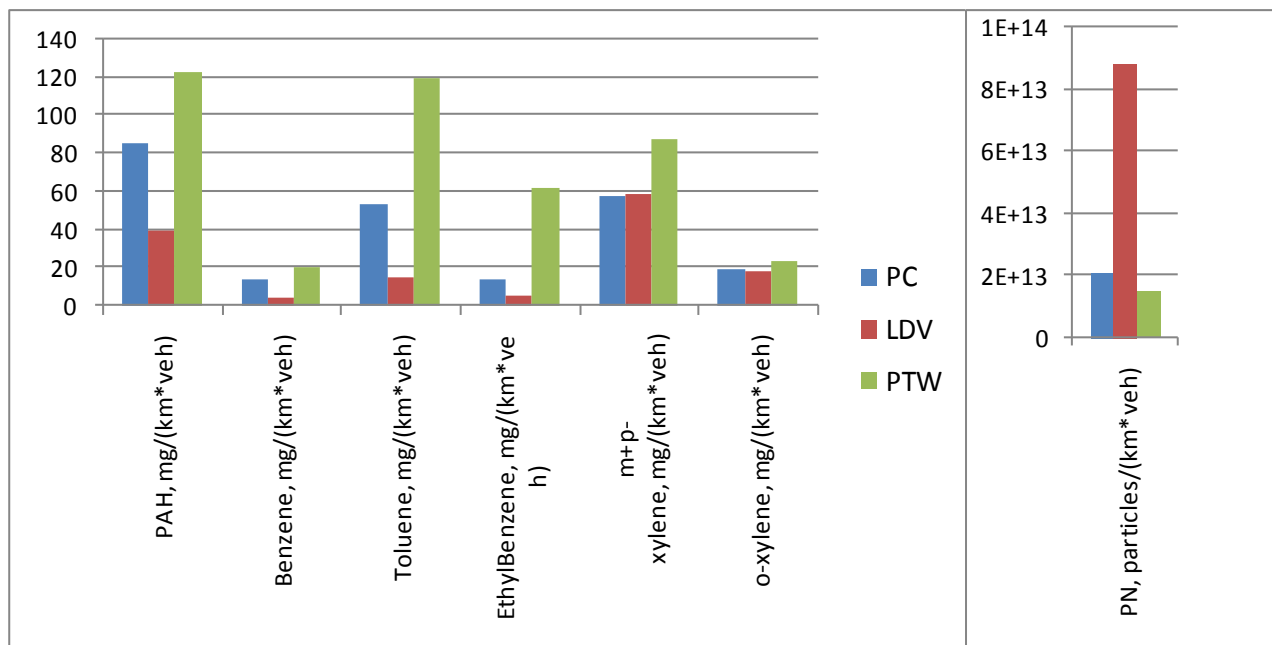


Figure 56. Emissions for several vehicle category

4.3.2 Air concentrations and vehicle emissions: quantitative correlation

The results of the comparison between the air concentrations and the emission rate of PN, PAHs and BTEX will be presented in this Section. The analysis was carried out by grouping data on the basis of sampling site; data referred to tunnel measurements such as those referred to urban traffic sites were collected in two groups: T and UT. The sub-urban type was not considered because, as previously highlighted, no traffic data are available for both S-UB and S-UT.

The Figure 57 shows the PN comparison. It reports the air concentrations vs the exhaust emission rates evaluated in T and UT sampling sites. This correlation was separately evaluated for each considered vehicle category (passenger cars, light duty vehicles, powered two wheelers) and also for the total vehicle flow. In each graph, linear correlation between data points, belonging to the same category, was estimated. The goodness of this correlation is explained by R^2 value, also reported in the graphs.

The PN correlation highlights a poor correspondence between the air concentration and the exhaust emission rate in UT sites. R^2 values, in fact, are always lower than 0,1. The tunnel correlation is quite good (R^2 almost 0.5). However, it has to be noted that data points of T sampling sites are too few to obtain a reliable correlation, in the sense that the analyzed traffic situations do not greatly differ in terms of traffic volume and composition. Measurements in fact were carried out during same daily period. This causes a low range of traffic variability which does not allow a study of air concentration dependence by traffic. Literature have demonstrated that the air particle number concentration should be positively correlated with the traffic flow, if traffic volume varies in a large interval (Pohjola et al., 2007, Pirjola et al., 2006).

The previous observation is valid for all pollutants measured in T sampling sites.

PN air and exhaust correlation seems not influenced by vehicle category. The best correlation for UT sampling sites was observed for PTW, even though the R^2 is very low, and it is the same for T sampling sites.

When analyzing PAH air and exhaust correlation (Figure 58), the poorness of data is even more evident than PN case study. The increasing linear correlation, in fact, is not visible in most PAH cases. Data, distributed in these graphs, do not follow a clear trend.

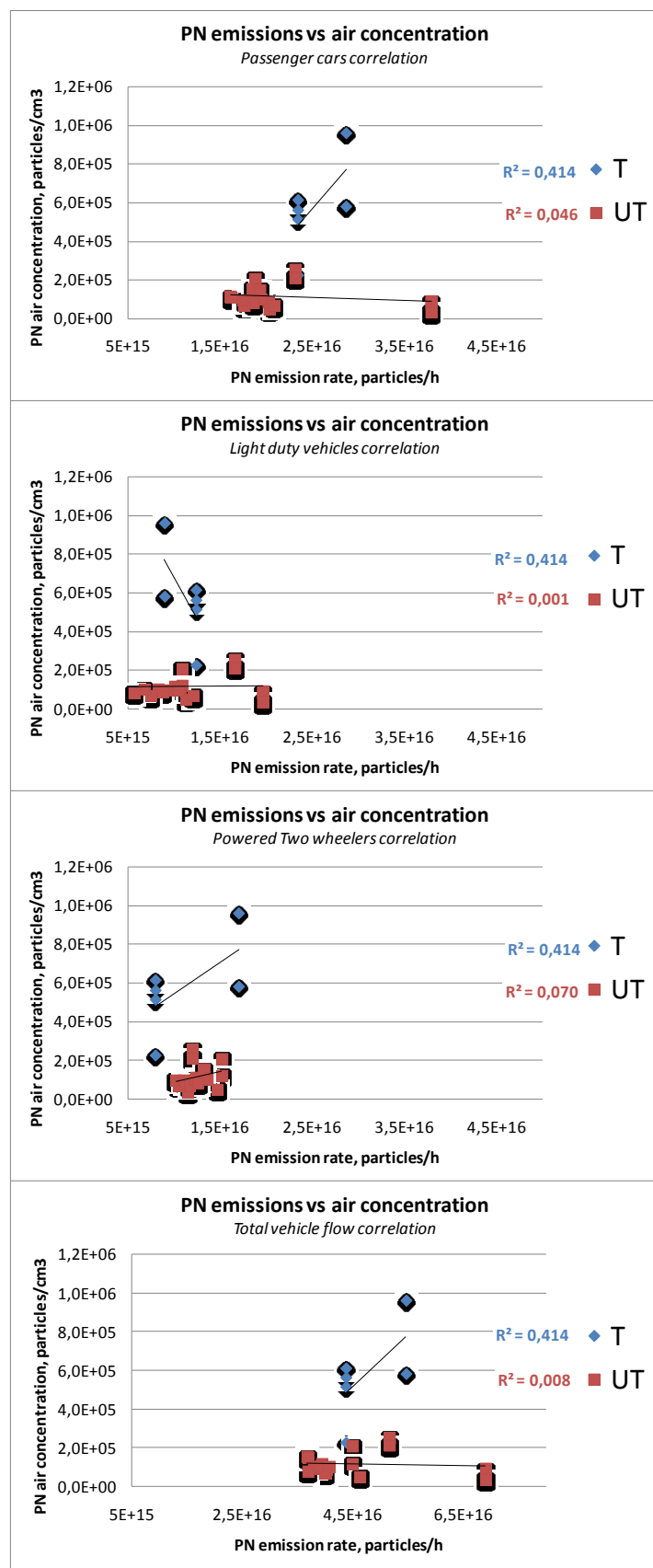


Figure 57. Comparison between exhaust emission rates and air concentrations for PN

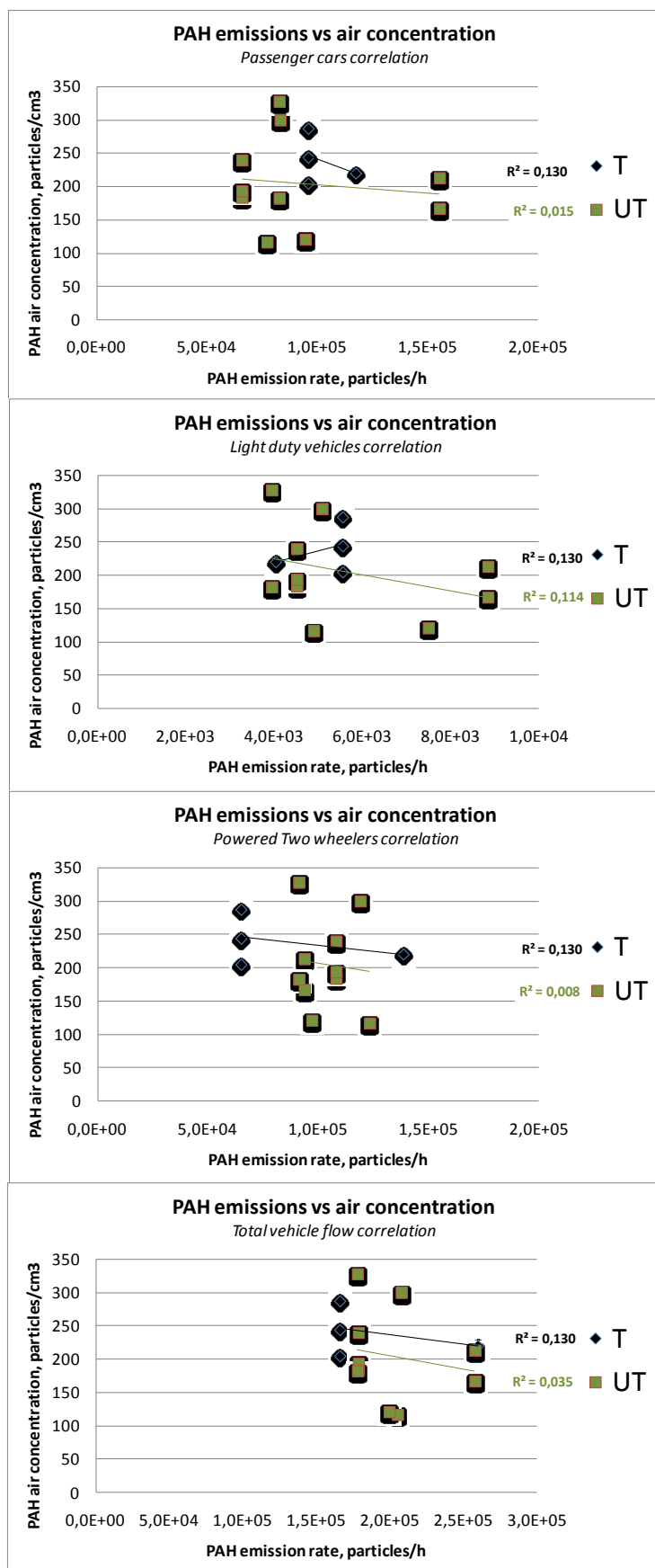


Figure 58. Comparison between exhaust emission rates and air concentrations for PAHs

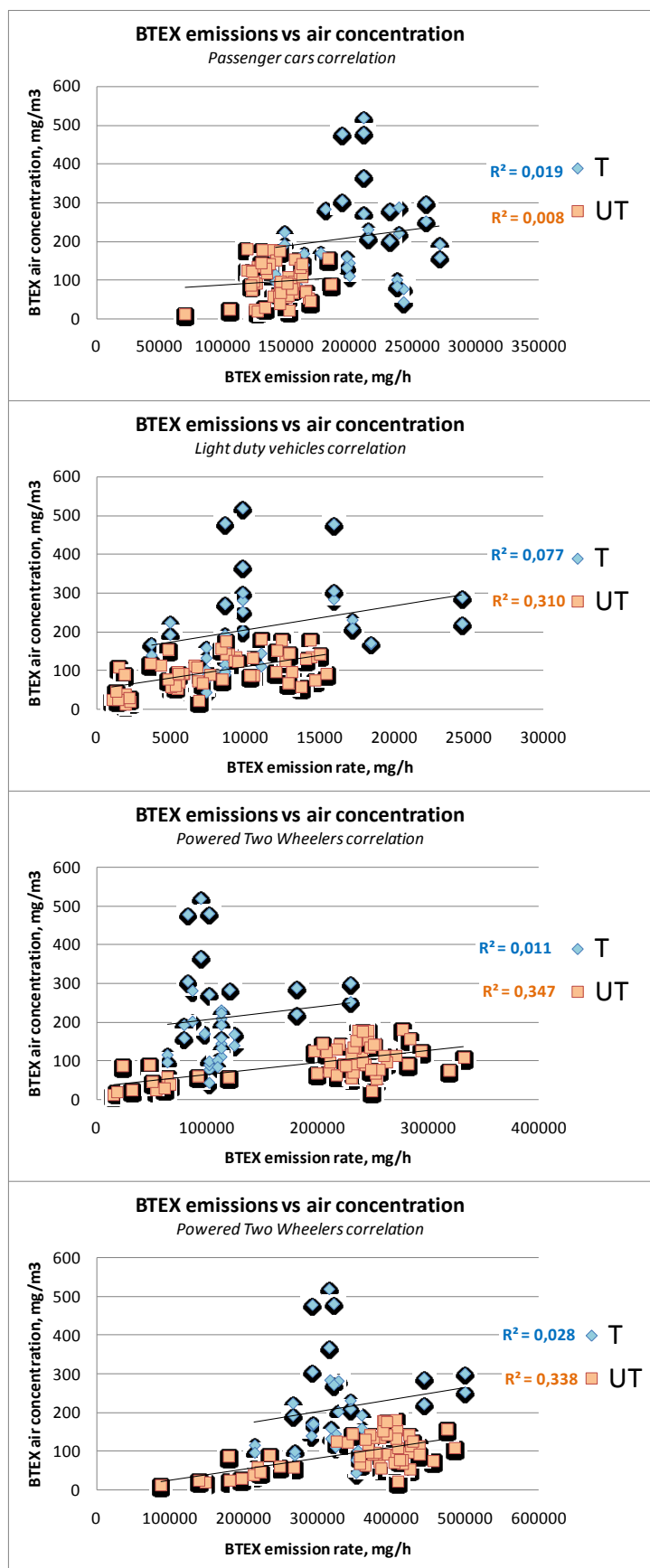


Figure 59. Comparison between exhaust emission rates and air concentrations for BTEXs

The best correlation was found for BTEX (Figure 59). As it is visible from the figure, data available for this compound class are more numerous than PAHs and PN. The correspondence between the BTEX air concentration and the exhaust emissions is always characterized by an increasing trend. It has to be noted that the correlation referred to UT site is better than that of T site; the reason probably lies in the low variability of traffic parameters, already mentioned. The highest R^2 evaluated for UT sites was estimated for PTW category.

In conclusion, the quantitative analysis carried out to correlate the emissions by road traffic with the air concentration levels in two sampling sites (tunnel and urban traffic) has showed not satisfactory results, in the sense that in most cases it was not possible to find a linear monotonic correlation between the two quantities. This expected behaviour derives from the hypothesis that all pollutants emitted in the atmosphere from road transport follow the same fate. This hypotheses should be more realistic inside the tunnel where no other pollution sources are present, the concentrations are much higher compared to ambient air, photochemical reactions are absent and mass transport can be neglected. Therefore concentration levels under the tunnel are strictly connected to vehicle emissions; but it is obviously far from reality in open site, because each species is characterized in air by a own residential time, an own chemical reactivity. Moreover, the same compound is subjected to the weather parameters, such as temperature, humidity and wind, that could greatly influence the air concentration. This aspect was not considered within this research activity.

Moreover, a great uncertainty is introduced in this estimation by the traffic composition and the emission factors. Although the traffic grouping in passenger cars, light-duty vehicles and two-wheelers was really monitored, the vehicle composition of each category in terms of fuel type and type approval stage was assumed to be equal to that provided by transport statistic studies. It is evident that it is an assumption and that the real composition should be very different. As already highlighted, the emission factors used for the estimation of the emission rate are not complete; strong hypotheses were needed for covering all the lack of data.

All these aspects contribute to make weak the quantitative correlation between the exhaust emissions and the air pollution.

More reliable correlations come from a qualitative analysis of pollutants measured in air and at the exhaust. These observations will be reported in the following section.

4.2.3 Air concentrations and vehicle emissions: qualitative correlation

Concerning the particulate correlation between ambient air and exhaust emissions, the more interesting aspect regards the particle size distribution. The influence of vehicle exhaust on the particle size distribution measured in air is strongly dependent by the sampling site.

The size distribution measured in open sites is decreasing when moving from small to large dimensions. Inside the tunnel, instead, the distribution becomes modal with the peak positioned on the second ELPI dimensional stage (almost 50 nm). This last distribution is more similar to the exhaust one. In other words, in the tunnel sites, characterized by a high PN concentration, the air particle size distribution corresponds to the exhaust emissions, whereas in the open sites characterized by a lower PN concentration the distribution is dominated by the finest particles. The different distributions are showed in Figure 60.

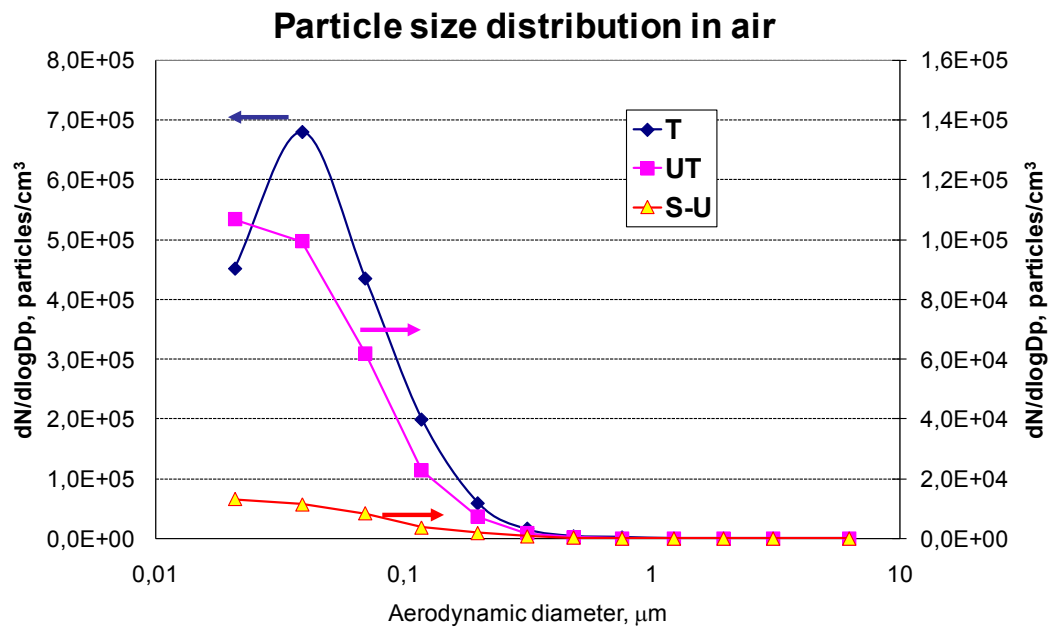


Figure 60. Particle size distribution in air

In order to highlight the difference between the air and exhaust particle dimensional distribution, the relative contribution of the 12 ELPI collecting stages to the total amount of particle number was evaluated.

The Figure 61 and Figure 62 report the results of this computation carried out in air concentrations and in the emission rate of real circulating vehicle fleet; the two figures are relative to the tunnel site and urban traffic site, respectively. N1,...N12 means the particle number collected on 1st12th ELPI filters. The first four dimensional stages covering the PM_{0,1} particulate, assume the highest values in the plot; they represent, in fact, more than 90% of the total particle number. It is interesting to note that the finest particles collected on the first and second stages are more abundant in ambient air of both sites. The data points relative to N1 and N2 are, in fact, positioned over the bisector. The contribution from third and fourth stages is instead higher in vehicle exhaust.

This analysis confirm the observation already done that the ambient air particulate has a great contribution of volatiles, at the expense of larger particles. As showed in the right side of the figures, in fact, also the larger particles collected on stages from 8 to 12 are more abundant in vehicle exhaust than in air.

In conclusion, it is not easy to obtain a good correlation between the particle number in air and at the exhaust. The reason probably lies in the complexity of particulate composition which makes this pollutant very variable and sensitive, especially regarding the size distribution. This is particularly true for the volatiles.

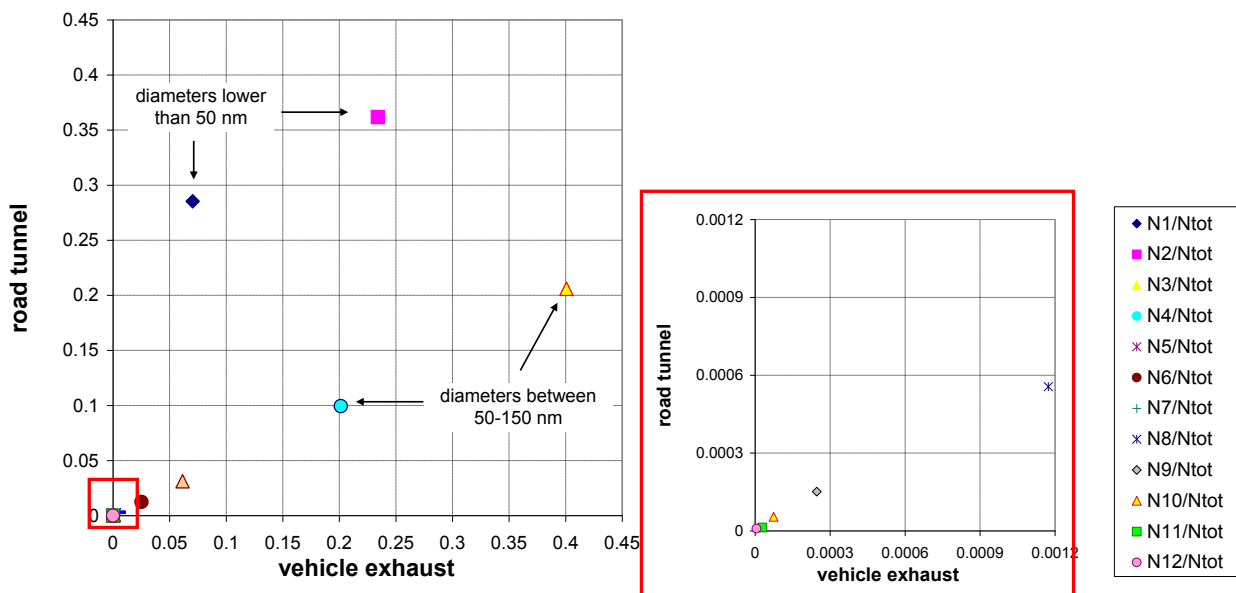


Figure 61. Ambient air and vehicle exhausts PN relative distribution in tunnel site

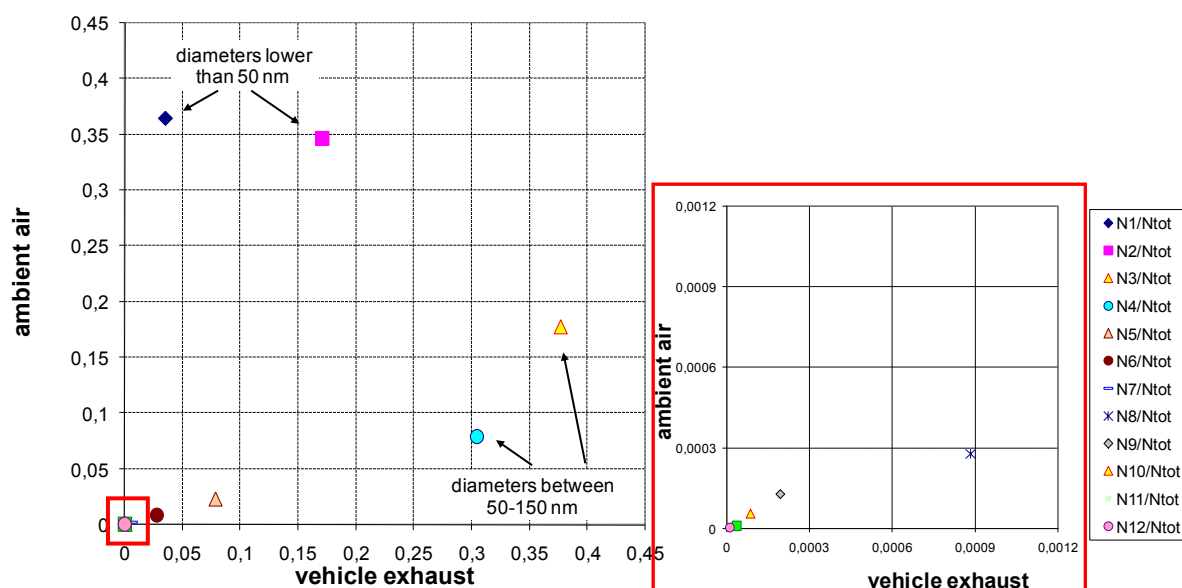


Figure 62. Ambient air and vehicle exhausts PN relative distribution in urban traffic site

The qualitative correlation between the traffic pollution source and the effect on air concentration was evaluated also for total bounded particulate PAHs. A common approach in the literature to correlate PAHs air concentration with the traffic uses the so called “diagnostic ratio”. This method is aimed to find specific PAHs ratios which have similar values or trends in ambient air and at the exhaust. In the most cases, it wants to identify the source of pollution (for example traffic or industrial exhaust) and inside the traffic source to distinguish the different contribution by the several categories (for example diesel or gasoline fuelled vehicles).

A literature review on the theme has allowed to identify a lot of diagnostic ratios suggested by different authors. The Table 13 lists the most common diagnostic ratios and the relative references.

The diagnostic ratios reported in the table were evaluated starting from the experimental data collected in all the sampling sites of ambient air monitoring and in all the vehicle exhausts. Results did not provide useful information about the pollution source. As example, the Figure 63 reports Fluorantene/(Fluoranthene+Pyrene) diagnostic ratio evaluated in the different sampling sites and at the exhaust of some vehicle technology. This ratio is commonly used to discriminate between gasoline or diesel motorization. At the exhaust of diesel vehicles fluotanthene to pyrene ratio is lower than that measured at the exhaust of gasoline fueled vehicles. The comparison between the absolute values of this diagnostic ratio evaluated in ambient air (blue bars in the figure) and in vehicle exhausts (grey bars) does not confirm this statement. Exhaust ratios are, in fact, very similar and also close to those evaluated in ambient air (values ranging between 0,45-0,5). Indeed, the

diagnostic ratio approach seems to be not suitable for identifying the pollution sources. The poor results obtained are explained by the more complex after-treatment devices for pollutant abatement applied in the last years at the vehicle exhaust. The good working of these devices causes the loss of information about the fuel type. The distribution of polycyclic aromatics which reflect the fuel used for engine combustion is totally changed by oxidation catalyst which almost totally removes the PAHs tailpipe emissions. For this reason, it becomes very difficult to use PAHs ratios to discriminate among diesel and gasoline fueled vehicles. It should give more results to use diagnostic ratio approach for differentiating among air pollution sources (traffic, industrial, natural). But in our cases, the air pollution in all the sampling sites is strongly influenced by road traffic.

| DIAGNOSTIC RATIO | Ref. |
|--|-------------------------------|
| indeno[1,2,3-cd]pyrene/(indeno[1,2,3-cd]pyrene+benzo[ghi]perylene) | <i>Ravindra et al., 2006</i> |
| benzo(a)pyrene/(benzo(a)pyrene+chrysene) | <i>Guo et al., 2003</i> |
| benzo(a)pyrene/benzo(ghi)perylene | <i>Park et al., 2002</i> |
| indeno[1,2,3-cd]pyrene/benzo[ghi]perylene | <i>Caricchia et al., 1999</i> |
| CPAHs(fluorene+pyrene+benzo(a)anthracene+chrysene+benzo(b)fluoranthene+benzo(k)fluoranthene+benzo(a)pyrene+indeno(1,2,3-cd)pyrene+benzo(ghi)perylene)/TPAHs | <i>Ravindra et al., 2008</i> |
| Pyrene/benzo(e)pyrene | |
| Pyrene/benzo(a)pyrene | <i>Neilsen et al., 1996</i> |
| Fluoranthene/pyrene | |
| Phenanthrene/(phenanthrene+anthracene) | <i>Guo et al., 2003</i> |
| Fluoranthene/(fluoranthene+pyrene) | <i>Manoli et al., 2004</i> |

Table 13. Common PAHs diagnostic ratios

In this application, more information come from the comparison of air and exhaust relative distributions of single PAH.

The found correlation is reported in Figure 64 and Figure 65. The figures report the ratios between the single PAH and the sum of all PAHs evaluated for ambient air concentration and vehicle emission rates, in road tunnel and in urban traffic site, respectively. The linear correlation fits the data points with an R^2 of 0,6 for road tunnel and 0,62 for urban traffic site.

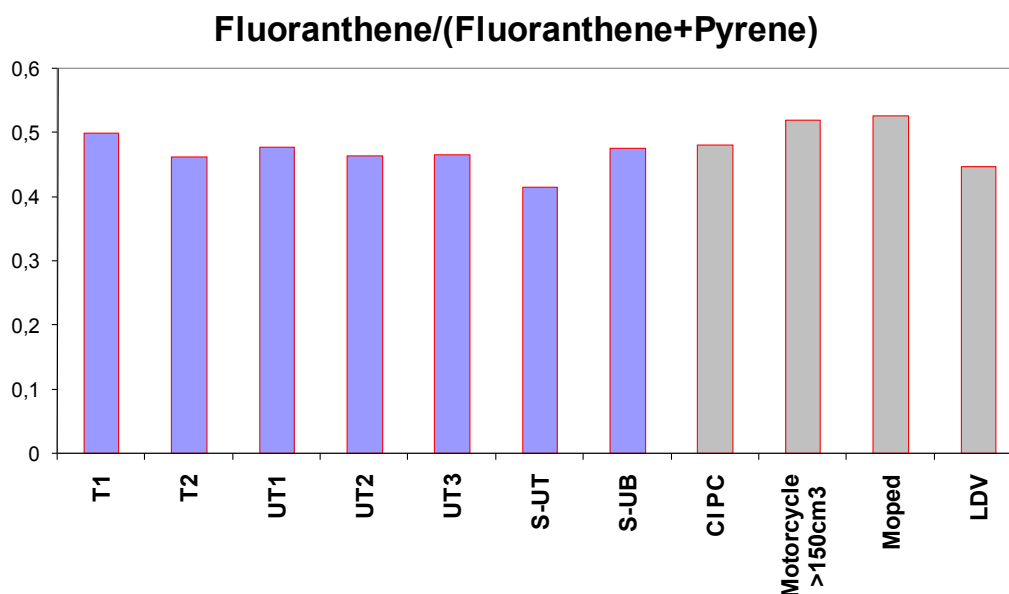


Figure 63. Fluoranthene/(Fluoranthene+Pyrene) diagnostic ratio

By analyzing road tunnel correlation, it is possible to state that benzo(a)pyrene is more abundant in air than in the exhausts. The other compounds that deviate from the linear correlation are fluoranthene, benzo(e)pyrene, indeno(1,2,3-cd)pyrene, 3,4-benzofluorene and dibenzo(a,e)pyrene. The not-perfect correlation of these last two compounds is mainly due to the very low concentrations measured in both ambient air and exhaust particulate.

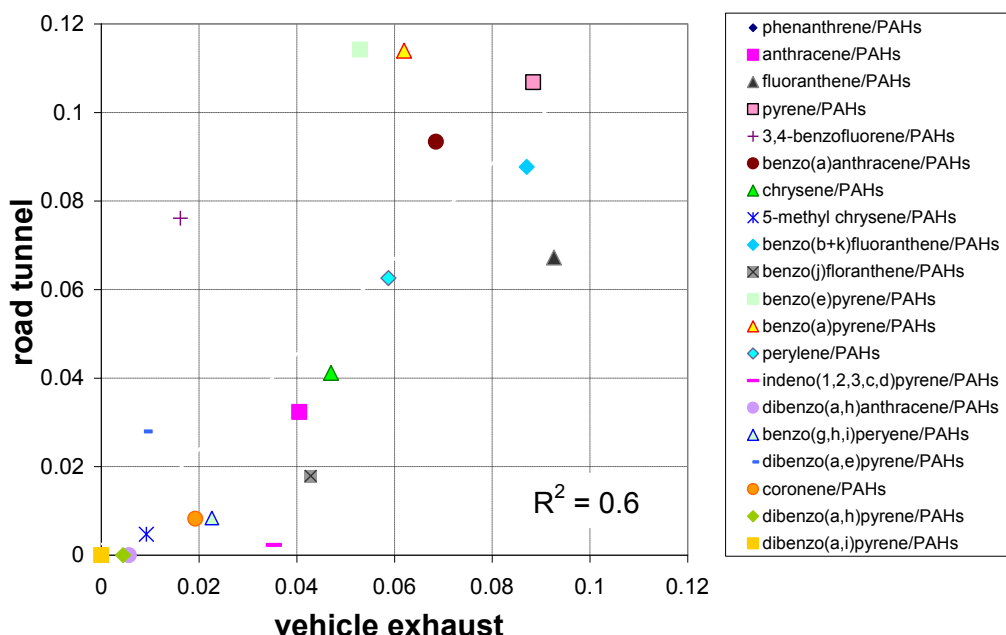


Figure 64. Single PAHs ratios in road tunnel air concentrations and in vehicle emission rates

When looking at urban traffic correlation, the correlation is better than that evaluated for road tunnel. Only coronene to total PAHs ratio is quite far from linearity; its relative concentration in air is, in fact, higher than that in vehicle exhaust.

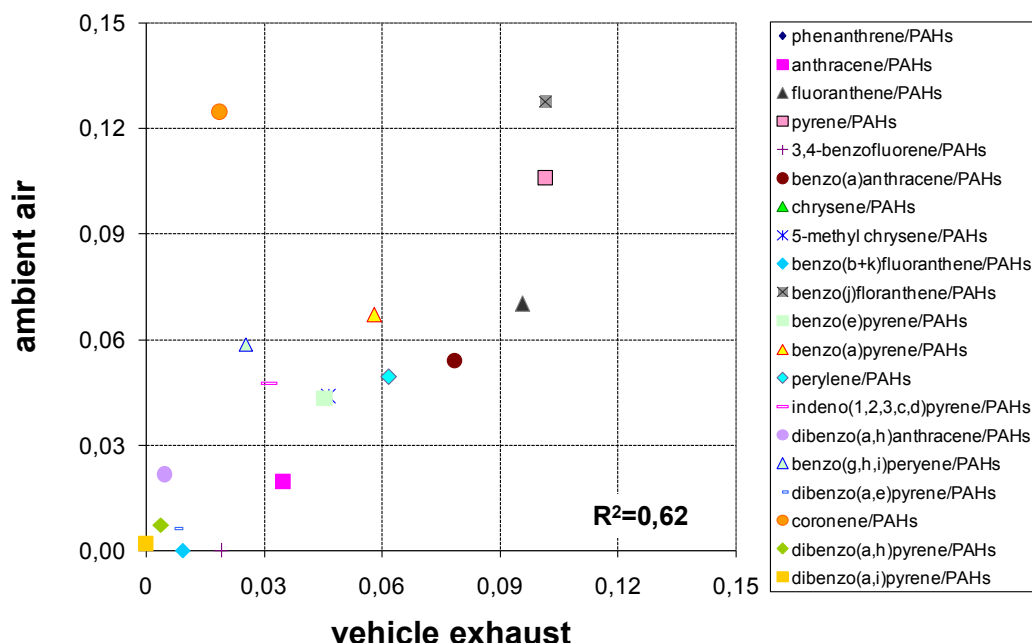


Figure 65. PAHs ratios in urban traffic air concentrations and in vehicle emission rates

The qualitative correlation between the exhaust emissions and the air concentrations was also carried out for BTEXs. A common method for stating the BTEX source apportionment is to correlate the single compounds each others. A good correlation means that they come from the same pollution source.

This method applied to the experimental results leads to very good results. Figure 66 shows the correlation between the single compounds measured in the ambient air of tunnel T1 and urban traffic site UT2. R^2 of linear correlation are always higher than 0,78. This good correlation demonstrates that the BTEXs derive from the same source of traffic exhaust.

To confirm the strict relationship between the air concentrations and vehicle exhaust emission rate, Figure 67 and Figure 68 graph the relative ratios between the single compounds evaluated in both air and exhaust. The two figures are relative to tunnel T1 and urban traffic site UT2.

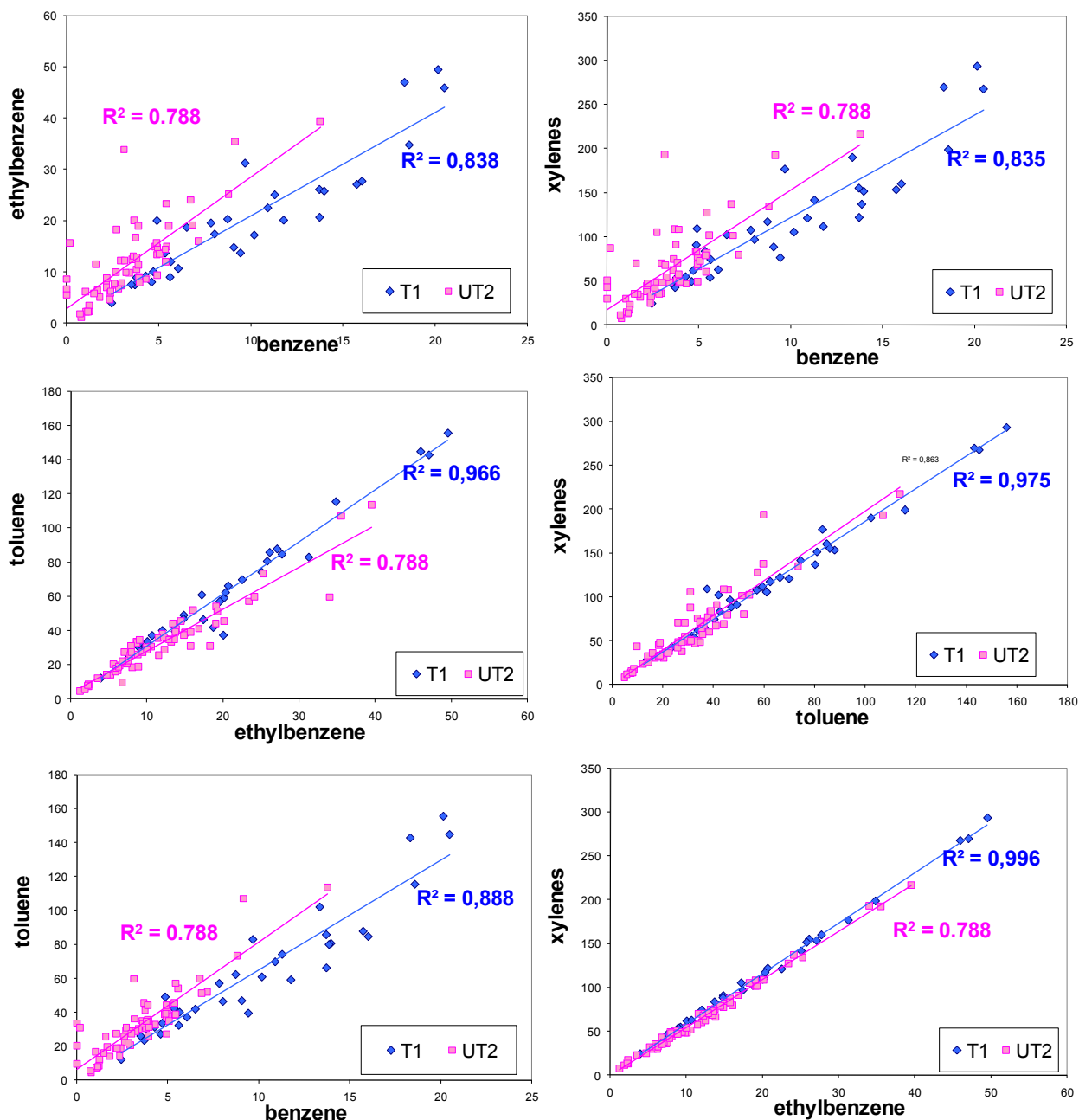


Figure 66. Single BTEX correlations in T1 and UT2 sampling sites

The figures report air values (measured in tunnel and urban traffic) on the y axis and vehicle exhaust ones on the x axis. The BTEXs in air are, obviously, well correlated with exhaust emissions if these ratios are similar. This happens in the most of the cases; R^2 of linear correlation are, in fact, almost 0,9. The not-perfect linearity is due to xylenes ratios; they are positioned in the upper zone of the graphs confirming the evidence that the concentration in air is higher than the contribution of estimated exhaust vehicle emissions.

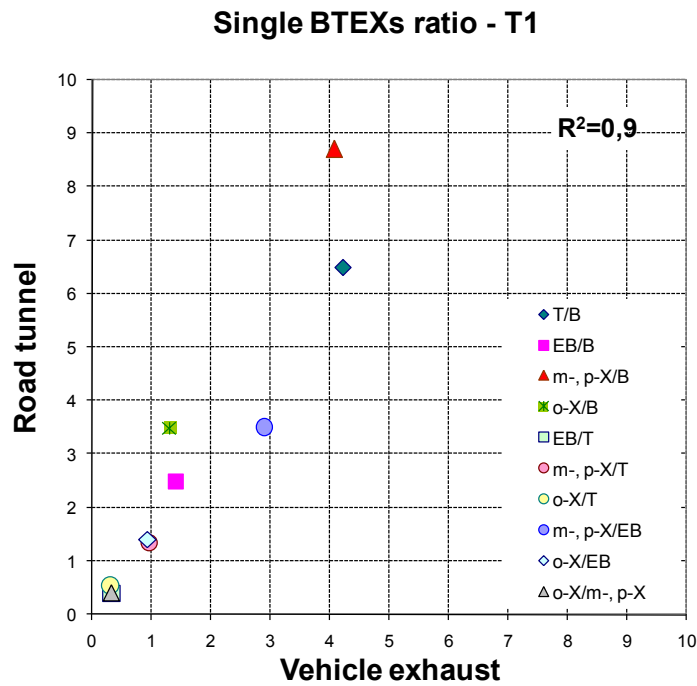


Figure 67. Correlation between BTEXs air concentrations and vehicle exhaust emissions in T1

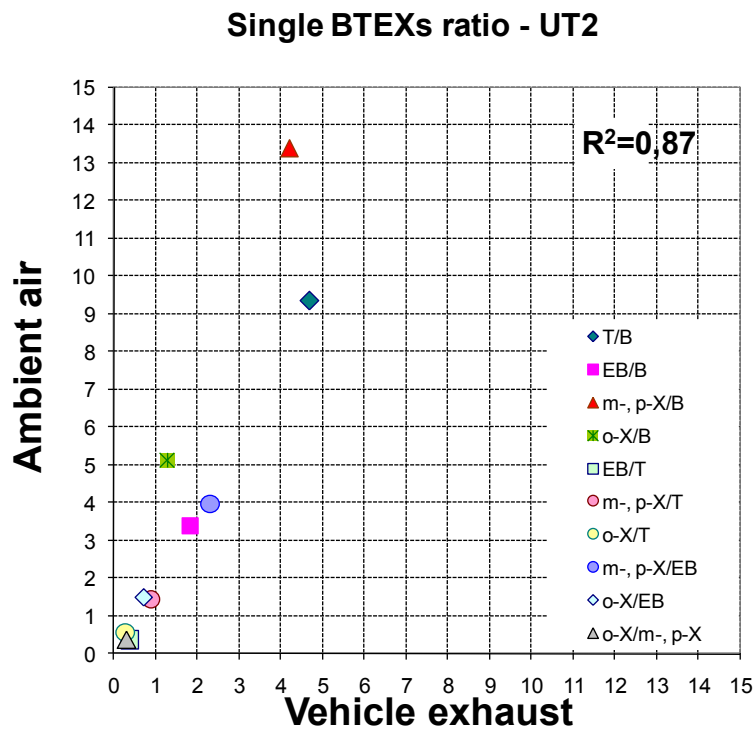


Figure 68. Correlation between BTEXs air concentrations and vehicle exhaust emissions in UT2

4.3.4 Conclusions about the correlation of air pollution with exhaust emissions

The quantitative correlation carried out between exhaust emissions derived from road traffic with the air concentration levels did not provide satisfactory results. Many aspects contribute to increase the uncertainty of this analysis. First of all, the number of observations is poor, especially for PN and PAHs case studies. Moreover, after the pollutants are emitted in the atmosphere, all the compounds do not follow the same fate because each species is characterized by a own residential time and an own chemical reactivity in air. Moreover, the same compound is subjected to the weather parameters, such as temperature, humidity and wind, that could greatly influence the air concentration. This aspect was not considered within this research activity. Moreover, the calculation of exhaust emission rates is greatly influenced by input traffic composition data and unregulated emission factors. The first uncertainness comes from the assumption that the traffic composition is equal to the statistical one. Moreover, the emission factors used for the estimation of the emission rate are not complete; strong hypotheses were needed for covering all the lack of data. More reliable correlations come from a qualitative analysis of pollutants measured in air and at the exhaust. A very good correlation ($R^2 > 0,6$) was observed between the PAH ratios and BTEX ratios evaluated in ambient air and in the exhaust emissions, confirming the pollution source of traffic exhaust. A weaker correlation was, instead, obtained for PN. The reason probably lies in the complexity of particulate composition which makes this pollutant very variable and sensitive, especially regarding the size distribution. This is particularly true for the volatiles.

Chapter 5

SUMMARY AND CONCLUSIONS

This experimental work has outlined the emission behaviour of different vehicles regarding particulate emissions in terms of mass, number and PAHs content; at the same time, air quality in different urban sites of Napoli was monitored for measuring particulate and BTEXs. The final goal was to correlate exhaust emissions with air pollution.

The most relevant evidence was that, taking into account the traffic composition in the urban area of Napoli, the PTWs cover a not negligible role in the particulate urban air pollution. Their emissions are, in fact, very close to those of the diesel vehicles not equipped with DPF which still represent the most particulate emissive motorization. The 2-stroke technology is more polluting than the 4-stroke one. The presence of the DPF is necessary to the diesel vehicles to comply with the actual Euro 5 standard limit. The PM emission reduction operated by DPF was, in fact, almost 93 %, making the PM emissions comparable with those of the SI passenger cars, whose engine technology is considered “clean” for particulate production and emissions.

In order to describe the particulate emissions as a function of the driving cycles, the average speed is an insufficient parameter; the whole kinematic of the driving cycle could strongly influence the particulate emissions. The experimental activity has observed that two driving cycles having very close average speed (UDC and Artemis Urban) produce very different particulate emissions. PN measured during the real and very dynamic Artemis Urban is almost 40% higher than that relative to type-approval UDC characterized by a long time in constant speeds.

Looking at particle size distribution, some differences were observed depending on vehicle category. Vehicle with the highest particle number emissions (mopeds and diesel w/o DPF) are characterized by a modal size distribution. In particular, the modal size distribution of mopeds peaks at almost 100 nm, that of diesel vehicles at almost 70 nm. The vehicle with a lower particle emissions (SI and motorcycle) are characterized by a bi-modal size distribution (first peak at almost 30 nm or lower and second in 80-120nm range). For these vehicle categories, in fact, the nucleation mode becomes evident. The bimodal particle size distribution is explained by a lower carbon

particle content, belonging to the accumulation mode, that does not enhance the volatile condensation on particle surface. In absence of a sufficient particle surface for condensation, volatiles remain in nucleation mode. The very low particulate emissive category, represented by diesel vehicle equipped with DPF, show a bimodal distribution only during tests with highest PN emissions. In the other tested conditions measured values are very low and close to the detection limit of measuring instrument.

The chemical analysis of particulate size collected by ELPI has marked that the major contribution of PAHs is given by particle smaller than 1 μm (PM1) which also corresponds to the dimensional range where the particle number distribution is included. An high percentage of PAHs (between 30 and 50%) is represented by carcinogenic compounds. The sum of low and middle molecular weight PAHs represents almost 60-80% of the total PAHs.

Simultaneously at the exhaust measurements, monitoring of ambient air quality was carried out in 7 urban site of Napoli, including two road tunnels, all having a quite high traffic flow (between 2000-3000 vehicles/h). The road tunnels present the highest particle number concentration ($5-8 \times 10^5$ particles/ cm^3), followed by the urban traffic sampling sites (almost 10^5 particles/ cm^3) and the sub-urban ones (almost 10^4 particles/ cm^3). The three concentration levels reflect also three different particle size distribution. In particular, the road tunnel size distribution measured is slightly different in the sense that, although modal, it peaks at almost 50 nm; those measured in urban and sub-urban sites, instead, have the peak on the first dimensional stage. The analysis of ambient particle distributions measured in all the sampling sites states that almost the 95% of total particle number is represented by particles with the diameter lower than 100 nm; the 100% of the particles has dimensions lower than 1 μm . In other words, ambient air particulate present the majority of particle number with a dimensions lower than 0.1 μm , the particle surface mainly developed in the accumulation mode (0.1-1 μm) and volume and mass divided between the accumulation and coarse (diameters higher than 1 μm) modes. Ambient air PM1 calculated by ELPI, assuming particle density of 1 g/cm^3 , agrees with PM2,5 measured by air quality monitoring station of Napoli. This implies that the hypothesis about the particle density is not so far from the real value for the ambient aerosol.

The carcinogenic PAHs percentage in ambient air particle phase was almost the same of that measured in the vehicle exhaust (30-45% of total PAHs) with benzo(a)pyrene covering almost the 5%. Looking at PAHs size distribution in the three dimensional groups corresponding to the

nucleation, accumulation and coarse modes, the highest content of PAHs was bounded to the particles in accumulation or coarse modes (diameter higher than 0,1 μm).

BTEXs air concentrations were measured in road tunnel and in open urban site. Although absolute concentration in road tunnels are almost twice than those relative in open site, the relative distribution of single compound is the same in two sampling sites: more abundant components are toluene and the sum of m- and p- xylene, followed by ethylbenzene, o-xylene and benzene with the minimum concentration value. Benzene measured in road tunnel atmosphere largely exceeds the air standard limit.

The ambient air concentrations were correlated, in a quantitative way, with exhaust emission rates produced by the real monitored traffic. This analysis was carried out for BTEXs, PAHs, and particle number, in both road tunnel and urban traffic sites. The emission rate calculation needed of the deep traffic characterisation taken by statistical data relative to Comune di Napoli and of the pollutant emission factors, mainly taken by results obtained within this research activity because of poor availability of data. Both assumptions contribute to make weak this quantitative correlation where results are not satisfactory. Many aspects contribute to increase the uncertainty of this analysis. First of all, the number of observations is poor, especially for PN and PAHs case studies. Moreover, all the compounds emitted in the atmosphere do not follow the same fate because each species is characterized by a own residential time and an own chemical reactivity. Moreover, the same compound concentration is subjected to the weather parameters, such as temperature, humidity and wind, that could greatly influence the air concentration. This aspect was not considered within this research activity. More reliable correlations come from a qualitative analysis of pollutants measured in air and at the exhaust. A very good correlation ($R^2 > 0,6$) was observed between the PAH ratios and BTEX ratios evaluated in both ambient air and exhaust emissions, confirming the pollution source of traffic exhaust. The deviation from linearity in BTEX correlation is due to xylenes ratios: the air concentration are higher than the contribution of exhaust vehicle emissions. This discrepancy is explained by a lack of emission data for this compound especially at the exhaust of PTWs. The not-perfect correlation of PAHs compounds is mainly due to the very low concentrations measured in both ambient air and exhaust particulate. The worst correlation was, instead, obtained for PN. The reason probably lies in the complexity of particulate composition which makes this pollutant very variable and sensitive, especially regarding the size distribution of volatiles. The correlation states, in fact, that the finest particles (diameters lower than 50 nm) are more abundant in road tunnel air. The contribution from larger particles is instead higher in vehicle exhaust. In other

words, the ambient air particulate has a great contribution of volatiles, at the expense of larger particles.

5.1 Future developments

The influence of traffic vehicle exhaust on pollution air in urban areas should greatly improve by enriching the poor existing data base of unregulated emission factors. The correlation between exhaust emissions and air concentrations needs of the knowledge of in-use emission factors. In other words, the laboratory emission factors could be not useful for estimating the real traffic emission rates, if they are referred to kinematic parameters different from real ones. A laboratory study for characterising unregulated emission factors of different vehicle categories, varying driving cycle parameters, should aid the computation of real exhaust emissions. Moreover, another improvement should be introduced by a more precise characterisation of traffic, in terms of fuel type and type-approval stage.

Because the weakest results were obtained for particulate correlation, additional tests are needed for finding a more accurate methodology of PM and PN measurements in both air and exhausts.

Moreover, it should be very interesting to deeply chemically characterise the particulate in order to find a tracer of vehicle exhaust pollution source which affects the ambient air quality.

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